# ORGANOTITANIUM AND NIOBIUM CHEMISTRY

## I. STRUCTURE AND REACTIVITY OF A TITANIUM ETHYLENE COMPLEX

## II. REACTIVITY OF DECAMETHYL NIOBOCENE DERIVATIVES

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Abstract

The synthesis and X-ray diffraction study of bis(pentamethylcyclopentadienyl) ethylene titanium (I) are reported. This complex represents the first example of an isolable ethylene adduct of a group IV metal, a key intermediate in Ziegler-Natta olefin polymerization schemes. While treatment of I with ethylene leads to only traces of polymer after months, I participates in a wide range of stoichiometric and catalytic reactions. These include the catalytic conversion of ethylene specifically to butadiene and ethane and the catalytic isomerization of alkenes. Detailed studies have been carried out on the stoichiometric reactions of I with nitriles and alkynes. At low temperatures, nitriles react to form metallacycloimine species which more slowly undergo a formal 1, 3-hydrogen shift to generate metallacycloeneamines. The lowest energy pathway for this rearrangement is an intramolecular hydrogen shift which is sensitive to the steric bulk of the R substituent. The reactions of I with alkynes yield metallacyclopentene complexes with high regioisomer selectivity. Carbonylation of the metallacyclopentene $(\eta\text{-}C_5Me_5)_2\overline{TiC(CH_3)=C(CH_3)CH_2CH_2}$ under relatively mild conditions cleanly produces the corresponding cyclopentenone and $[C_5(CH_3)_5]_2Ti(CO)_2$. Compounds derived from $CO_2$ and acetaldehyde have also been isolated.

The synthesis and characterization of bis-($\eta$-pentamethylcyclopentadienyl)niobium(III) tetrahydroborate (II) are described and a study of its temperature-dependent proton NMR spectroscopic behavior is reported. The complex is observed to undergo a rapid intramolecular averaging process at elevated temperatures. The free energy of

activation, $\Delta G^{\ddagger} = 16.4 \pm 0.4$ kcal/mol, is calculated. The reinvestigation of a related compound, bis($\eta$-cyclopentadienyl)niobium(III) tetrahydroborate, established $\Delta G^{\ddagger} = 14.6 \pm 0.2$ kcal/mol for the hydrogen exchange process. The tetrahydroborate complex II reacts with pyridine and dihydrogen to yield $(\eta\text{-}C_5Me_5)_2NbH_3$ (III). The reactivity of III with CO and ethylene is reported.

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# Chapter I

## The Olefin Chemistry of Decamethyltitanocene and the Structure of Bis Pentamethylcyclopentadienyl Ethylene Titanium (II)

## Introduction

Organotitanium chemistry has been a very active area of research since mixtures of $TiCl_4$ and trialkylaluminum were first reported as active catalysts for the polymerization of ethylene and the formation of highly ordered polymers of the $\alpha$-olefins.[1,2] In light of the scientific and commercial importance of olefin polymerization, significant effort has been directed towards the elucidation of the mechanism(s) of Ziegler-Natta type catalysis.[2] Although a number of substantially different mechanisms have been formulated,[3] the reaction is generally believed to occur via coordination of an olefin to an alkyltitanium complex which then undergoes olefin insertion (or alkyl

$$L_nTi\text{-}R \rightarrow \underset{\downarrow}{\overset{=\!=}{L_n}}Ti\text{-}R \rightarrow L_nTi\text{-}CH_2CH_2R \rightarrow \text{etc.}$$

migration) to generate a new alkyltitanium species.[2,4] A key feature common to virtually all schemes is the proposed intermediacy of a titanium $\pi$-olefin complex, a species which, in fact, has never been observed.

While titanium olefin complexes have not been characterized, some evidence for olefin complexes of zirconium does exist. Addition of ethylene to $Zr(CH_2SiMe_3)_4$ (liquid) produces low concentrations of an olefin adduct of unknown structure.[5] Dimeric complexes in which an olefin bridges two formal Zr(III) moieties have been isolated, e.g., $[(\eta\text{-}C_5H_5)_2ZrCl]_2(\mu\text{-}CHPhCHPh)$[6] and $[ZrCl_3(PEt_3)_2]_2(\mu\text{-}CH_2CHMe)$; the structure of one such complex, $[(\eta\text{-}C_5H_5)_2ZrCl]_2(\mu\text{-}CH_2CH_2)$, has been reported.[8] An ethylene complex, $(\eta\text{-}C_5Me_5)_2Zr(\eta\text{-}C_2H_4)$, is strongly

implicated as an important but unobserved intermediate in the ethylene-promoted reductive elimination of isobutane from $(\eta\text{-}C_5Me_5)_2ZrH(CH_2CHMe_2)$[9] while existence of the corresponding propene and butene intermediates is suggested by the reactivity and fluxional behavior observed for the zirconium allyl hydride complexes, $(\eta\text{-}C_5Me_5)_2ZrH(\eta\text{-}CH_2CHCHR)$ where R = H, Me.[10]

Our investigations on the interactions of olefins with bis(pentamethylcyclopentadienyl)titanium (II) have led to the preparation of one olefin complex, $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$, and are detailed below.

## Experimental Section

General Considerations. All manipulations were performed using glove box or high vacuum line techniques. Argon, nitrogen, and hydrogen were purified by passage over MnO on vermiculite and activated Linde 4 Å molecular sieves. Solvents were purified by vacuum transfer, first from $LiAlH_4$, then "titanocene."[11] Benzene-$d_6$ and toluene-$d_8$ (Aldrich, Stohler) were dried over molecular sieves and vacuum transferred from "titanocene." Ethylene, propene, cis-2-butene, 1-butene, trans-2-butene, 1-hexene and HCl (anh) were freeze-pump-thaw degassed at least twice at -196°. Carbon monoxide was used directly from the cylinder. Ethylene-$^{13}C_2$ (90% $^{13}C$, Merck, Sharp, and Dohme) and ethylene-$d_4$ (98% D, Stohler) were freeze-pump-thaw degassed at -196° and distilled at -78°. Methyl iodide (MCB) was vacuum transferred from $CaH_2$.

Propene-$d_6$ (> 99% D) was prepared by reduction of $(CD_3)_2CO$ (Stohler, 99.5% D) to $(CD_3)_2CDOD$ using $NaBD_4$ (Stohler, 99% D)/NaOD in $D_2O$ (Stohler, 99.8% D) followed by dehydration over $D_2O$-washed $Al_2O_3$ at 300°C.[12] Methyl isocyanide was synthesized by literature procedures,[13] freeze-pump-thaw degassed, and vacuum transferred from molecular sieves. $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ and $(\eta\text{-}C_5Me_5)_2Ti(CH_3)_2$ were prepared by previously reported methods.[14] $(\eta\text{-}C_5Me_5)_2TiCl_2$ was prepared by the procedure given in reference 14a with the following modifications: $LiC_5Me_5$ was used in place of $NaC_5Me_5$, and the resulting mixture of $TiCl_3/LiC_5Me_5$ in THF was heated at reflux for three days.

Proton, $^{2}H$, and $^{13}C$ NMR spectra were recorded using Varian T-60 and EM-390, JEOL FX90Q, and Bruker WM-500[15] spectrometers. Spectra were taken in benzene or toluene solutions, and data are referenced to $Me_4Si$ at 0 δ. Infrared spectra were obtained using Beckman IR-12 and 4240 spectrophotometers; spectra of solids were recorded as nujol mulls using KBr plates; spectra of gases were measured using a 10 cm path length cell (NaCl windows) fitted with a stopcock and ball joint for attachment to a vacuum line. Mass spectrometer data were obtained using a DuPont 21-492 mass spectrometer and a Kratos MS-25 GC-MS. Hydrocarbon gases were analyzed using a Varian 940 gas chromatograph equipped with a thermal conductivity detector using a 120 foot 13% DBT (dibutyltetrachlorophthalate) on Chromosorb W column. Molecular weights were determined cryoscopically or by vapor phase osmometry. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories, Germany.

Procedures. $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ (2). Sodium amalgam (300 g, 0.9% w/w) was added via syringe to an argon-blanketed toluene slurry (150 mL) of $(\eta\text{-}C_5Me_5)_2TiCl_2$ (3.40 g, 8.73 mmol). The argon atmosphere was replaced with ethylene and maintained at ca. 700 torr while the mixture was stirred 72 h. The resulting yellow-brown solution was filtered, and the toluene and excess $C_2H_4$ were removed in vacuo to yield the crude product. Recrystallization from petroleum ether afforded 2.5 g (80%) of bright green 2. Anal. Calcd for $C_{22}H_{34}Ti$: C, 76.28; H, 9.89. Found: C, 76.14; H, 9.84. Molecular weight (osmometry in $C_6H_6$): 334 (calcd 346). IR: 3657 (m), 3042 (s), 2981 (s)*, 2963 (m)*, 2935 (m)*, 2904 (vs)*, 2858 (s)*, 2721 (m), 1490 (m), 1435 (m)*,

1377 (vs)*, 1163 (w), 1127 (w), 1077 (vs), 1060 (w), 1023 (s), 875 (m), 802 (w), 749 (m), 668 (m), 627 (w), 612 (w), 581 (2), 538 (m), 500 (w), 465 (w), 413 (s) $cm^{-1}$ (*measured in Halocarbonoil). $^1H$ NMR: $C_5(C\underline{H}_3)_5$, 1.68 (s); $C_2\underline{H}_4$, 2.02 (s). $^{13}C$ NMR (mult., $^1J_{C-H}$ in Hz) $\underline{C}_5(CH_3)_5$, 119.8 (s); $C_5(\underline{C}H_3)_5$, 11.9 (q, 125); $\underline{C}_2H_4$, 105.1 (t, 143.6).

$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}^{13}CH_2{}^{13}CH_2)$ ($\underset{\frown}{2}\text{-}^{13}\underline{C}_2$). Ethylene-$^{13}\underline{C}_2$ (0.267 mmol) was condensed at -196° onto a frozen solution of $[(\eta\text{-}C_5Me_5)_2Ti]_2N_2$ (90 mg, 0.13 mmol) in 5 mL toluene. The mixture was warmed to 25° and stirred 20 min. The deep blue solution was frozen at -196° and the $N_2$ removed <u>in vacuo.</u> The mixture was warmed to 25° and stirred an additional 10 min. Solvent was removed <u>in vacuo</u> from the light green solution, yielding 90 mg $\underset{\frown}{2}\text{-}^{13}\underline{C}_2$ (96%). IR: 3682 (vw), 3664 (vw), 3033 (s), 2725 (m), 1493 (m), 1165 (w), 1061 (s), 1047 (vs), 1024 (s), 867 (m), 805 (m), 666 (m), 641 (m), 615 (w), 591 (w), 570 (m), 551 (w), 490 (m), 415 (s), 375 (w) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2D_4)$ ($\underset{\frown}{2}\text{-}\underline{d}_4$). Ethylene-$\underline{d}_4$ (0.3 mmol) and 5 mL toluene were condensed at -196° onto $[\eta\text{-}C_5Me_5)_2Ti]_2N_2$ (50 mg, 0.075 mmol). The mixture was warmed to 0° and stirred 20 min at that temperature. Toluene, $N_2$, and excess $C_2D_4$ were removed <u>in vacuo.</u> The green crystalline $\underset{\frown}{2}\text{-}\underline{d}_4$ was stored at -30° to minimize H-D scrambling. IR: 3675 (vw), 3620 (vw), 2722 (m), 2280 (m), 2190 (m), 2159 (m), 2078 (w), 2000 (w), 1979 (vw), 1965 (m), 1946 (w), 1731 (m), 1536 (vw), 1489 (m), 1185 (m), 1161 (w), 1146 (w), 1097 (m), 1023 (s), 932 (m), 902 (w), 637 (w), 625 (vw), 615 (w), 591 (w), 564 (w), 549 (vw), 515 (s), 458 (m), 395 (m), 367 (w) $cm^{-1}$.

2 + CO. Excess CO (0.5 mmol) was partially condensed at -196° into an NMR tube containing a frozen solution of 2 (29 mg, 0.08 mmol) in 0.4 mL toluene-$d_8$. The tube was sealed and the reaction monitored between -78° and -20° by $^1H$ and $^{13}C$ NMR. The rate of formation of $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$ (4) and $C_2H_4$ appears to be limited by the solubility of 2 in cold toluene but the reaction was complete after 3 h at -30°.

2 + $CH_3NC$. Methyl isocyanide (0.11 mmol) was condensed at -196° into an NMR tube containing a frozen solution of 2 (37 mg, 0.11 mmol) in 0.4 mL toluene-$d_8$. The tube was sealed and the reaction monitored between -78° and -10°. After 1 h at -50°, the solution contained 0.5 eq unreacted 2, 0.5 eq $C_2H_4$, and 0.5 eq $(\eta\text{-}C_5Me_5)_2Ti(CNCH_3)_2$ (5) ($^1H$ and $^{13}C$ NMR). Above 0°, 5 was found to be unstable in solution or as a solid, decomposing to a number of unidentified products with liberation of some free $CH_3NC$. $^1H$ NMR: $C_5(C\underline{H}_3)_5$, 1.80 (s); $CNC\underline{H}_3$, 2.90 (s). $^{13}C$ NMR: $\underline{C}_5(CH_3)_5$, 106.2 (s); $C_5(\underline{C}H_3)_5$, 12.1 (q, 125); $CN\underline{C}H_3$, 38.3 (q, 140).

2 + $H_2$. Hydrogenation of 2 was carried out by a procedure similar to that given for 2 + CO. The formation of $(\eta\text{-}C_5Me_5)_2TiH_2$ (7) and $C_2H_6$ was complete after 2 h at -50°.

2 + HCl. Hydrogen chloride (0.208 mmol) was condensed at -196° into an NMR tube containing a frozen solution of 2 (34 mg, 0.10 mmol) in 0.3 mL toluene-$d_8$. The tube was sealed and immediately upon warming to -78°, a reaction occurred, yielding ethane and a purple-red solid identified as $(\eta\text{-}C_5Me_5)_2TiCl_2$ ($^1H$ NMR).

2 + $CH_3I$. Methyl iodide (0.58 mmol) was condensed at -78° onto a frozen solution of 2 (38 mg, 0.11 mmol) in benzene-$d_6$ (0.3 mL). The mixture was warmed to 80° for 90 min, yielding $(\eta\text{-}C_5Me_5)_2TiI(CH_3)$ (8) (ca. 90% pure) and ethylene (0.92 mol/mol 2, $^1$H NMR). A major impurity contaminating 8 was identified as $(\eta\text{-}C_5Me_5)_2Ti(CH_3)_2$ (6). Other attempts to prepare 8 resulted in materials which were 85-95% pure after recrystallization. $^1$H NMR (8): $C_5(CH_3)_5$, 1.86 (s); $CH_3$, -0.41 (s).

$(\eta\text{-}C_5Me_5)_2TiCl$ (9). Toluene-$d_8$ (0.8 mL) and ethylene (0.3 mmol) were condensed at -196° into an NMR tube containing 55 mg 1 (0.14 mmol) and 50 mg 2 (0.14 mmol). The tube was sealed and the sample heated at 85° for 1 h. The resulting slurry was dried in vacuo, yielding a deep blue solid (80 mg), identified by IR as the previously described[16] $(\eta\text{-}C_5Me_5)_2TiCl$. Paramagnetic 9 is also formed during the preparation of 2 by reduction of 1 and can be a contaminant in samples of 2. A toluene solution of 9 (0.06 mmol in 7 mL) was treated with ethylene (0.130 mmol) at 25° for 30 min, then cooled to -78° and stirred an additional 60 min. The residual gases were passed through two -78° traps and 0.133 mmol of gas was collected via a Toepler pump, condensed in a $LN_2$-cooled trap, and discarded.

2 + $C_2H_4 \rightleftharpoons (\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$ (10). Toluene-$d_8$ (0.5 mL) and ethylene (0.710 mmol) were condensed at -196° into a NMR tube containing 2 (22.2 mg, 0.0641 mmol) and ferrocene (67.4 mg, 0.364 mmol). The NMR tube was sealed and [2], [10], and $[C_2H_4]$ were measured by $^1$H NMR as a function of temperature from 25 to 75° (Figure 1). Since the equilibrium favors 2 + $C_2H_4$ over 10 at available

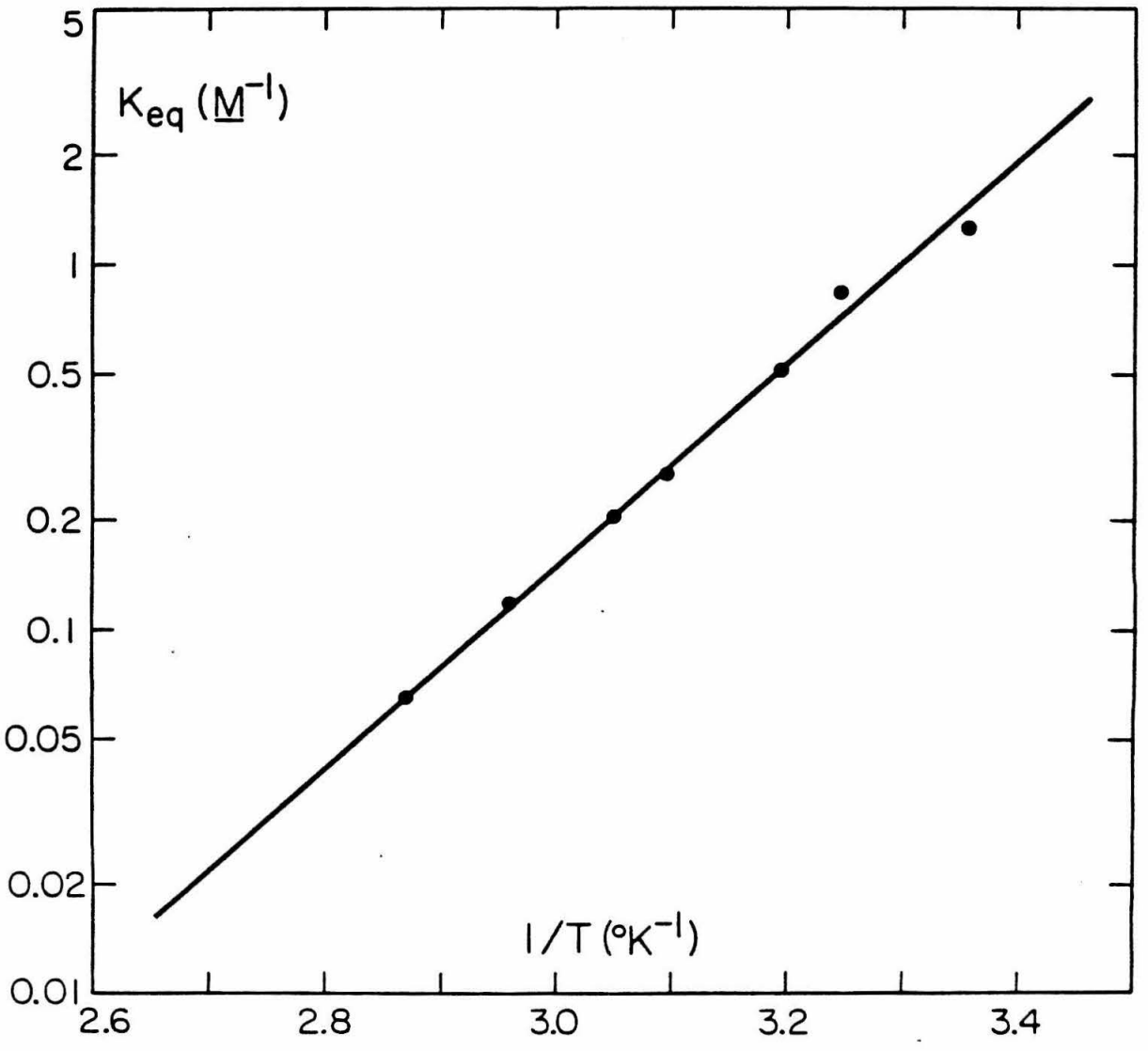



Figure 1. Temperature dependence of $\underset{\sim}{2} + C_2H_4 \rightleftharpoons \underset{\sim}{10}$.

[$C_2H_4$], 10 could not be isolated. The metallacyclopentane 10 was characterized by its chemical reactivity as well as $^1H$ and $^{13}C$ NMR spectroscopy. $^1H$ NMR: $C_5(C\underline{H}_3)_5$, 1.80 (s); $C\underline{H}_2(CH_2)_2C\underline{H}_2$, 0.60 (m); $CH_2(C\underline{H}_2)_2CH_2$, 1.72 (m). $^{13}C$ NMR: $\underline{C}_5(CH_3)_5$, 120.7 (s); $C_5(\underline{C}H_3)_5$, 12.3 (q, 125); $\underline{C}H_2(CH_2)_2\underline{C}H_2$, 62.4 (t, 123); $CH_2(\underline{C}H_2)_2CH_2$, 32.8 (t, 122); $^1J(C_\alpha\text{-}C_\beta)$ = 29 Hz.

2 + 10 + HCl. Toluene (50 mL) and ethylene (13.2 mmol) were condensed at -196° onto 2 (50.5 mg, 0.146 mmol) contained in a thick-walled glass vessel fitted with a Teflon needle valve. The mixture was allowed to warm to 25° and was stirred overnight. The resulting orange-brown solution was cooled to -78° and excess ethylene was removed in vacuo. Anhydrous HCl (0.784 mmol) was condensed at -196° onto a frozen solution of 2 and 10. The reaction occurred immediately upon warming the mixture to -78°. Residual gases were condensed at -196° onto a frozen solution of NaOH (120 mg) in 1 mL $H_2O$, and the mixture was warmed to 25°. The remaining gas was identified as a 60:40 mixture of ethane and butane ($^1H$ NMR).

Isomerization of 1-butene by 2. An NMR tube was charged with 0.5 mL of a benzene-$d_6$ stock solution containing 2 (61.6 ± 0.2 mg/mL, 0.178 M) and ferrocene (54.6 ± 0.7 mg/mL, 0.293 M) and cooled to -196°. 1-Butene (0.92 mmol) was condensed onto the frozen solution and the tube was sealed. The sample was heated in a 61° oil bath and the reaction was monitored as a function of time by $^1H$ NMR. Additional samples which contained varying amounts of 1-butene and added $C_2H_4$ were prepared and isomerized at 61°, 72°, and 81° (Figure 2).

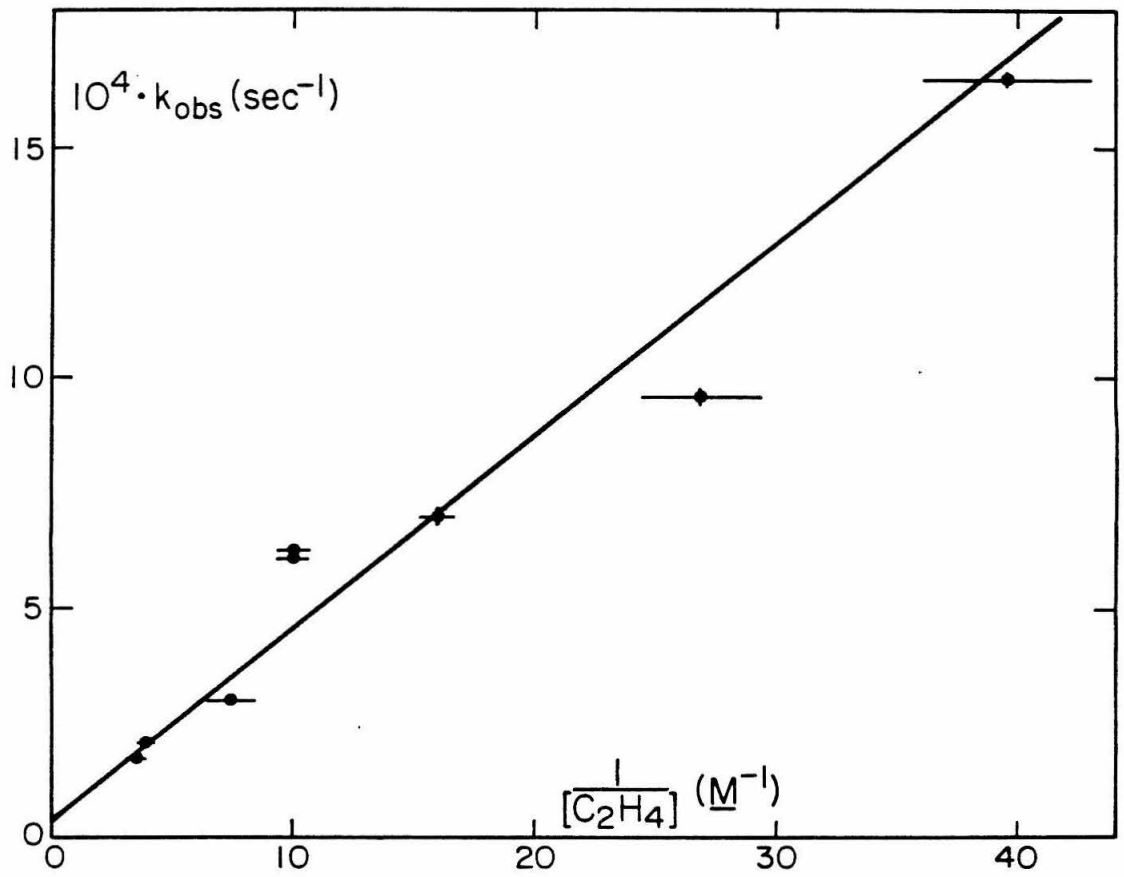



Figure 2. Ethylene concentration dependence of 1-butene isomerization reaction at 106°.

Isomerization of propene by 2. An NMR tube containing 2 (50 mg, 0.14 mmol), $C_3H_6$ (0.263 mmol), $C_3D_6$ (0.138 mmol), and $C_6H_6$ (0.40 mL) was sealed under vacuum and heated to 81°. The reactants were monitored for H-D exchange by $^2H$ NMR (13.7 MHz). Samples for monitoring the reaction at other temperatures as well as blanks were similarly prepared. In a separate experiment, the products of the reaction between 2 and $C_3D_6$ were analyzed by $^2H$ NMR and IR spectroscopy. The two methods were found to give similar results (±3%).

Conversion of ethylene to 1, 3-butadiene and ethane catalyzed by 2. Benzene-$d_6$ (0.5 mL), ethylene (0.543 mmol), and ethylene-$^{13}C_2$ (0.067 mmol) were condensed at -196° into an NMR tube containing 2 (60 mg, 0.17 mmol). Upon sealing the tube, the sample was warmed to 25° and monitored by $^1H$ and $^{13}C$ NMR. Over a ten month period, the intensities of the $C_2H_4$ and $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$ (10) resonances diminished as resonances identified as 1,3-butadiene and ethane appeared and slowly increased. The total concentration of titanium species, [2 + 10], remained constant throughout. The tube was opened under vacuum, the volatile contents passed through two -78° cold traps and 0.357 mmol gas (0.156 mmol $C_4H_6$ and 0.201 mmol $C_2H_6$ by $^1H$ NMR, MS) was collected via a Toepler pump. The remaining solid in the tube was washed with petroleum ether and filtered, affording ca. 1 mg polyethylene (IR).

A sample containing 1-butene (0.062 mmol), 2 (30 mg, 0.087 mmol), $C_2H_4$ (0.715 mmol) and toluene-$d_8$ (0.52 mL) was prepared and allowed to react at 25°. After five months, ethane and butadiene

(ca. 0.7 mmol each) were observed but no measurable change (< 3%) in [1-butene] was seen by $^1$H NMR.

Toluene (5.0 mL) and ethylene (17 mmol) were condensed onto 240 mg 2 (0.693 mmol) contained in a thick-walled glass vessel equipped with a Teflon needle valve. The mixture was warmed to 55 ± 3° and stirred at that temperature for 1620 h. The solution was cooled to 0°, and the residual gases were collected and identified as $C_2H_6$, $C_4H_6$, $C_4H_8$ and unreacted $C_2H_4$ (IR, GC-MS). The toluene solution containing 2 was removed in vacuo; 230 mg 2 was isolated along with 5 mg polyethylene.

X-Ray Structure Determination. Well-formed crystals of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ were obtained by cooling a saturated toluene solution from 55° to 25° over an 8 h period. The green, air-sensitive crystals were sealed in glass capillaries under argon to prevent decomposition. A series of Weissenberg and precession photographs ($CuK_\alpha$ and $MoK_\alpha$ radiation) indicated that the crystals possess 4/mmm Laue symmetry with the systematic absences h00, odd. The choice of space groups was thus restricted to the two tetragonal space groups, $P42_12$ and $P\bar{4}2_1m$. Unit cell dimensions were determined by least-squares fit of $\sin^2\theta/\lambda^2$ to fifteen reflections with $2\theta$ values between 10 and 40°. Crystal data are given in Table I.

A crystal 0.32 × 0.37 × 0.48 mm was mounted with its c axis slightly skew to the $\phi$ axis of a modified Syntex $P2_1$ automatic X-ray diffractometer. Intensities were measured for all ($+h$, $+k$, $\pm\ell$) reflections between 3 and 70° in $2\theta$ using $\theta$-$2\theta$ scans and a variable scan

Table I. Crystal Data

| $C_{22}H_{34}Ti$ | Tetragonal space group $P\bar{4}2_1m$ |
|---|---|
| a = 10.8621(4) Å | $\rho_{expt}$ = 1.15 ± 0.05 g·cm$^{-3}$ |
| c = 8.5008(5) Å | $\rho_{calc}$ = 1.147 g·cm$^{-3}$ |
| V = 1002.97(8) Å$^3$ | $\lambda(MoK_\alpha)$ = 0.71069 Å |
| Z = 2 | $\mu$ = 4.42 cm$^{-1}$ |

rate between 1.0 and 6.0° min$^{-1}$ using graphite-monochromated $MoK_\alpha$ radiation. The scan width varied linearly from 1.8° at $2\theta$ = 3° to 2.3° at $2\theta$ = 70° with 24 sec background counts measured before and after each scan. A variance $\sigma^2(I)$ was calculated for each reflection based on counting statistics and a term $(0.02\ S)^2$, where S is the scan count. The intensities of four check reflections measured every 100 reflections indicated that no crystal decomposition occurred during the data collection.

The intensities and variances of the 5347 reflections were corrected for Lorentz and polarization effects but not for absorption

($\mu$ = 4.42 $cm^{-1}$). The intensities from equivalent reflections, (+$\underline{h}$, +$\underline{k}$, ±$\underline{\ell}$) and (+$\underline{k}$, +$\underline{h}$, ±$\underline{\ell}$), were averaged, and sixty data for which $I < 0$ were assigned weights and $F^2$ equal to zero, leaving 1279 reflections in the working data set.

Solution and Refinement. The data were placed on an absolute scale by means of a Wilson plot, with scattering factors for Ti calculated by the method of Cromer and Waber and those for C and H by the method of Cromer and Mann.[17] Density measurements ($CCl_4/C_7H_8$)[18] indicated there are two molecules per unit cell. Without additional systematic absences, a Z value of 2 requires (i) mm or $\bar{4}$ molecular symmetry for space group $P\bar{4}2_1m$ or (ii) 4 or 222 symmetry for $P42_12$. A three-dimensional Patterson map was generated from which the titanium atoms were located at (0, $\frac{1}{2}$, 0.22) and ($\frac{1}{2}$, 0, -0.22), thus ruling out $\bar{4}$ and 222 as possible symmetry elements. The space group $P\bar{4}2_1m$ was selected since ($\eta$-$C_5Me_5)_2Ti(\eta$-$C_2H_4)$, in its eclipsed-ring conformation, possesses the necessary mm symmetry while $P42_12$ can only be accommodated by means of a four-fold disorder. This choice is justified by the successful solution of the structure.

Placement of the Ti gave an R index ($\Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.34. However, the titanium atom contributes only to the $\underline{h} + \underline{k} = 2n$ reflections and the resulting Fourier map exhibited additional symmetry. An ethylene carbon atom was located in the Fourier map and was used to phase all of the data in the space group $P\bar{4}2_1m$. Alternating structure factors calculations and difference Fourier maps revealed the positions of the remaining nonhydrogen atoms. Several cycles of

full-matrix least-squares refinement with anisotropic temperature parameters led to a structure with eclipsed $C_5Me_5$ rings (Figure 3a) and an R = 0.097.

At this point in the refinement, a difference Fourier map clearly revealed the coordinates of the ethylene hydrogen; however, numerous areas of residual electron density were found between adjacent carbon atoms of the $C_5Me_5$ ring which could not be attributed to methyl hydrogen atoms. Shallow minima were also found in the difference Fourier map at each of the ring carbon positions and it was apparent that the thermal parameters of these carbons were unusually large. These anomalies suggested that the $C_5Me_5$ rings are actually staggered and that the crystallographic mm symmetry is satisfied by a statistical disordering of the rings. In each of several attempts to continue the refinement of the ordered, eclipsed-ring structure, the R value decreased to a minimum between 0.084 and 0.087. A model having no $C_5Me_5$ carbons positioned on the mirror planes (Figure 3b) rapidly led to the correct structure.

Adopting the disordered ring model, isotropic refinement of the titanium, the ethylene carbon, and the ten carbon atoms of the $C_5Me_5$ ring, positioned from the Fourier map and assigned site populations = 0.5, gave an R = 0.12. The ethylene hydrogen was located from the difference Fourier map and positions for the fifteen methyl hydrogens were calculated (C–H = 0.95 Å). Following isotropic refinement of all nonhydrogen atoms (R = 0.071), the methyl hydrogens were positioned with the aid of difference Fourier maps, and a secondary

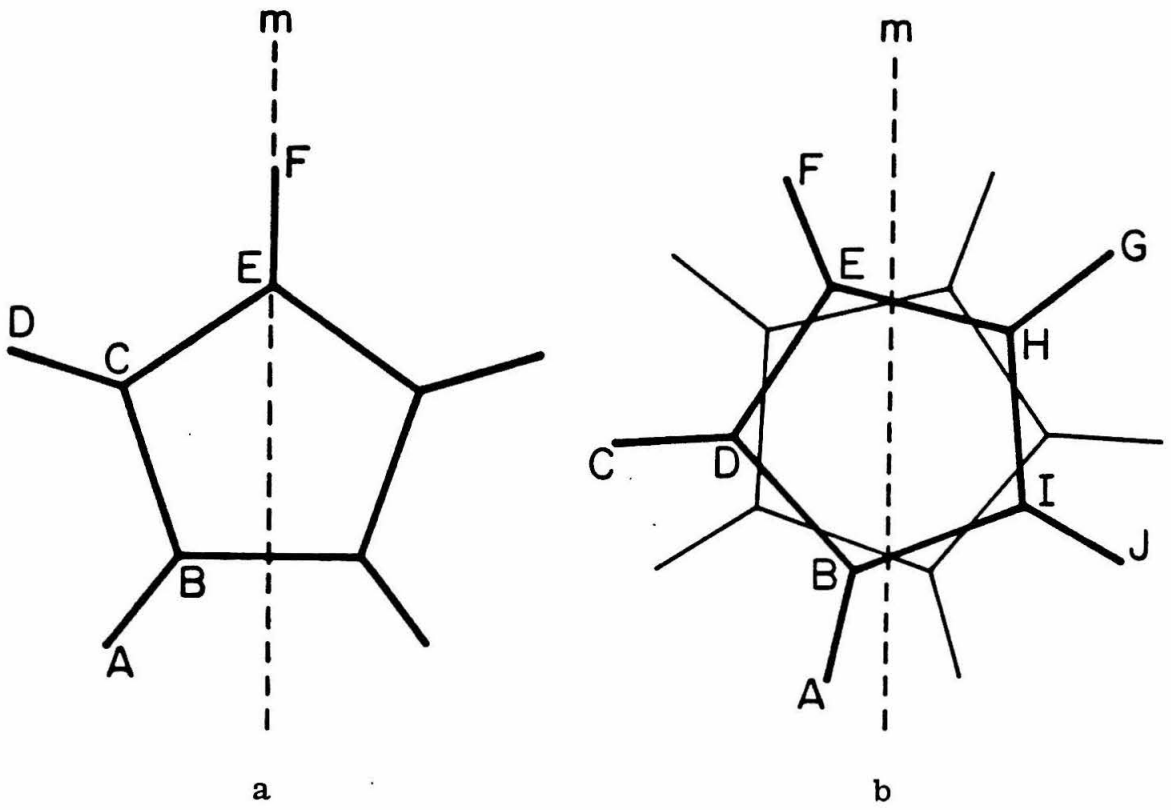



Figure 3. (a) Eclipsed ring model and (b) partially staggered ring model. Labels refer to crystallographically independent atoms.

extinction coefficient was introduced. All nonhydrogen parameters were anisotropically refined (3 cycles) along with the positional and isotropic thermal parameters of the ethylene hydrogen, giving an R value of 0.051. Full-matrix least-squares refinement rapidly converged after repositioning the methyl hydrogens from difference Fourier maps (the methyl hydrogen parameters were not refined). It should be noted that the $C_5Me_5$ rings are disordered due to a slight rotation about the Ti-ring centroid vector. The titanium atom and ethylene ligand are not disordered and are essentially unaffected by use of the staggered ring model in lieu of eclipsed ring geometry: C–C, 1.438 vs. 1.443 Å; Ti–C, 2.160 vs. 2.173 Å.

Final parameters are listed in Table II and give an R index of 0.050 and goodness-of-fit index, $[\Sigma w(F_o^2 - s^2F_c^2)^2/(N-P)]^{\frac{1}{2}}$, of 2.06 where s is the scale factor, N = 1279 data, and P = 106 parameters. In the final cycle of refinement, no parameters shifted by more than 0.7 $\sigma$. Except for a peak of 0.7 e/Å$^3$ located at the Ti position, no residual electron density greater than 0.4 e/Å remained in the final difference Fourier map.

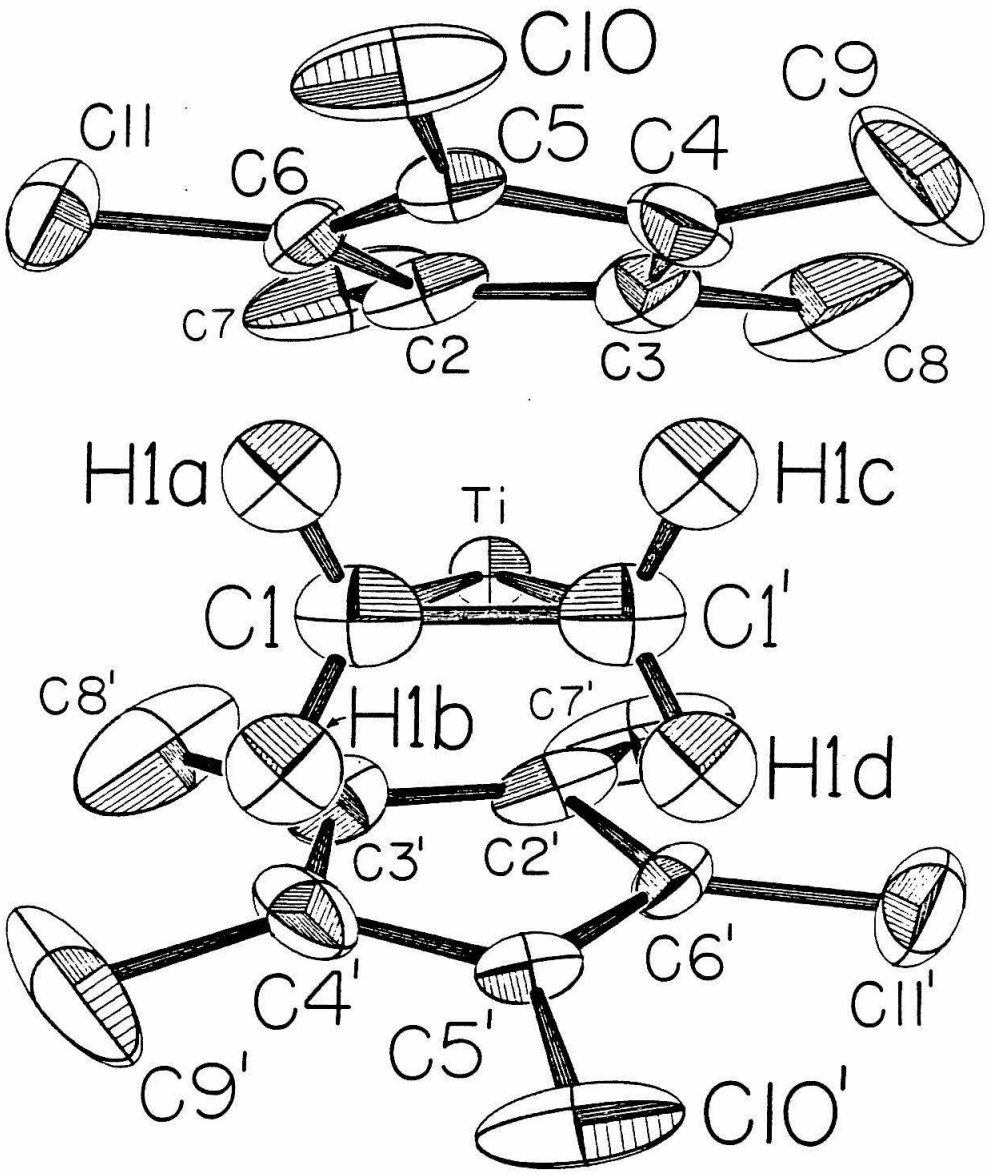



**Figure 4. Structure of 2 showing labelling scheme.**

## Results and Discussion

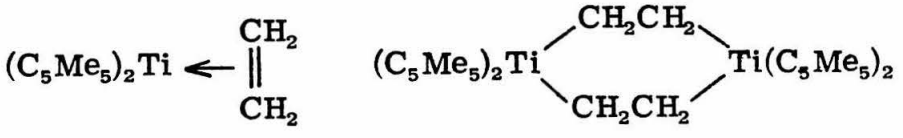
Synthesis and Characterization of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$. Sodium amalgam reduction of $(\eta\text{-}C_5Me_5)_2TiCl_2$ (1) in toluene under ca. 700 torr of ethylene affords emerald green $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ (2) in high yield (>80%). Alternately, the treatment of $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (3) with

$$(C_5Me_5)_2TiCl_2 + 2\ Na + C_2H_4 \xrightarrow[3\ d]{25^\circ} (C_5Me_5)_2Ti(C_2H_4) + 2\ NaCl \qquad (1)$$

ethylene rapidly and quantitatively produces 2 and $N_2$. Utilizing $C_2D_4$ in the latter procedure yields $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2D_4)$ (2-$d_4$), which is found

$$[(C_5Me_5)_2Ti]_2N_2 + 2\ C_2D_4 \xrightarrow[20\ min]{0^\circ} 2\ (C_5Me_5)_2Ti(C_2D_4) + N_2 \qquad (2)$$

by IR and NMR to undergo H-D exchange between the $C_2D_4$ and the $CH_3$ groups of the $C_5Me_5$ ligands ($t_{\frac{1}{2}} \simeq 24$ h at 25°). Spectroscopic and molecular weight data strongly suggest a monomeric titanium(II) $\pi$-olefin structure (A) for 2 rather than a dimeric structure with bridging ethylenes (B). The monomeric structure of 2 has been confirmed by




A B

single crystal X-ray diffraction techniques.

Structure of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$. The molecular structure of 2 is shown in Figure 4, a stereoscopic view in Figure 5, and a stereoscopic view of the unit cell in Figure 6. The molecule consists of a dihapto ethylene ligand coordinated in the equatorial plane of a "bent sandwich" decamethyltitanocene fragment.

The skeletal geometry about the titanium can be viewed as trigonal planar, similar to the structures of $(\eta\text{-}C_5H_5)_2MX$ compounds.[19,20] Alternately, it can be considered analogous to the numerous pseudotetrahedral $(\eta\text{-}C_5H_5)_2MX_2$ structures, with the two carbon atoms of the ethylene and the two $C_5Me_5$ ring centroids defining the vertices of a distorted tetrahedron. While the distortion from idealized trigonal or tetrahedral coordination, as measured by the ring centroid-Ti-ring centroid angle, is greater than that typically found for unsubstituted bis(cyclopentadienyl)titanium complexes, the value of 143.6(4)° observed for 2 (R-Ti-R′, Table III) compares favorably with those found for other $(\eta\text{-}C_5Me_5)_2Ti$ derivatives: 137.4(1)° for $(\eta\text{-}C_5Me_5)_2TiCl_2$,[21] 139.2° for $(\eta\text{-}C_5Me_5)_2Ti(CH_3)(OC)_3Mo(\eta\text{-}C_5H_5)$,[22] 145.7(3)° for $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$,[20] and 147.9° for $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$.[23] The large R-Ti-R angle in 2 is attributed, at least in part, to steric crowding due to the bulky $C_5Me_5$ ligands.

The single crystallographically independent pentamethylcyclopentadienyl ring is planar and is bonded to the Ti with a small tilt ($\delta$ = 2.2(3)°, Table V). The $C_{ring}$-$C_{ring}$ and $C_{ring}$-$C_{methyl}$ distances vary over a small range (1.376(14) - 1.432(15) and 1.478(10) - 1.534(12) Å, respectively) while the Ti-$C_{ring}$ distances vary over a wider range (2.353(8) - 2.464(10) Å, Table IV). These variations are typical of the

Table II. Final Refined Atom Parameters (coordinates $\times 10^4$, $U_{ij} \times 10^3$)[a,b,c]

| Atom | X | Y | Z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Tl | 0 | 5000 | 2206.4(6) | 37.3(1) | 37.3 | 31.9(2) | 2.1(6) | 0 | 0 |
| C1 | 468(2) | 5468 | 4603(3) | 74(1) | 74 | 38(1) | 12(2) | -10(1) | -10 |
| C2 | 1325(6) | 4188(7) | 197(8) | 50(5) | 102(10) | 29(2) | 31(6) | -4(2) | -9(3) |
| C3 | 454(7) | 3290(7) | 610(8) | 55(3) | 74(6) | 61(5) | 9(3) | -1(4) | -28(4) |
| C4 | 674(14) | 2880(12) | 2149(10) | 81(5) | 40(3) | 102(9) | 10(3) | 45(8) | 5(6) |
| C5 | 1712(11) | 3565(11) | 2706(6) | 46(5) | 60(7) | 49(2) | 17(6) | -6(3) | 2(3) |
| C6 | 2048(9) | 4364(11) | 1526(9) | 27(2) | 56(3) | 51(4) | 2(2) | 0(3) | -8(4) |
| C7 | 1627(6) | 4619(8) | -1406(6) | 103(4) | 239(10) | 53(3) | 98(6) | 40(3) | 40(4) |
| C8 | -421(6) | 2653(9) | -549(13) | 89(5) | 190(9) | 246(12) | 37(5) | -45(5) | -175(9) |
| C9 | 18(14) | 1805(6) | 2944(12) | 212(13) | 43(3) | 268(11) | -4(6) | 154(14) | 13(6) |
| C10 | 2350(7) | 3283(8) | 4214(6) | 116(7) | 179(11) | 64(3) | 93(8) | -8(3) | 17(4) |
| C11 | 3113(6) | 5231(10) | 1721(9) | 47(3) | 97(5) | 152(6) | -17(3) | 9(4) | -30(6) |
| H1a | 1287(16) | 5182(21) | 4942(21) | 5.66(49)[d] | | | | | |

a. The final scale factor is 0.7659(19).

b. The final value of the secondary extinction g is $1.77(22) \times 10^{-6}$.[34]

c. The form of the anisotropic temperature factor is $\exp[-2\pi^2(\underline{h}^2\underline{a}^{*2}U_{11} + \cdots + 2\underline{k}\underline{\ell}\underline{b}^*\underline{c}^*U_{23})]$.

d. The form of the isotropic temperature factor is $\exp[-B(\sin^2\theta/\lambda^2]$.

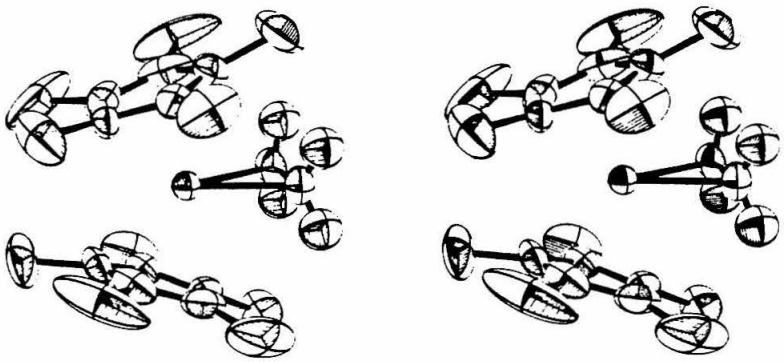


Figure 5.

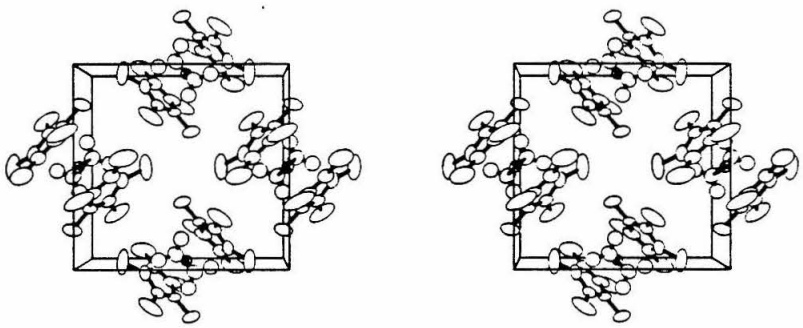


Figure 6.

Table III. Intramolecular Angles (degrees)

| | | | |
|---|---|---|---|
| C1-Ti-C1′ | 38.9(1) | C7-C2-C3 | 126.9(6) |
| C1-Ti-R | 107.9(3) | C7-C6-C6 | 125.5(7) |
| C1-Ti-R′ | 106.4(3) | C8-C3-C2 | 124.8(7) |
| R-Ti-R′ | 143.6(4) | C8-C3-C4 | 124.2(8) |
| R-Ti-E | 108.2(3) | C9-C4-C3 | 125.2(10) |
| | | C9-C4-C5 | 128.3(10) |
| Ti-C1-C1′ | 70.6(1) | C10-C5-C4 | 123.0(9) |
| Ti-C1-H1a | 114.5(10) | C10-C5-C6 | 129.4(8) |
| C1′-C1-H1a | 114.5(12) | C11-C6-C2 | 127.7(8) |
| H1a-C1-H1b | 119.0(16) | C11-C6-C5 | 121.3(8) |
| C6-C2-C3 | 105.8(7) | R-C2-C7 | 167.2(8) |
| C2-C3-C4 | 109.8(8) | R-C3-C8 | 170.7(9) |
| C3-C4-C5 | 106.1(9) | R-C4-C9 | 174.4(12) |
| C4-C5-C6 | 107.2(9) | R-C5-C10 | 172.3(10) |
| C5-C6-C2 | 110.9(8) | R-C6-C11 | 176.6(10) |

R = $C_5Me_5$ ring centroid; E = Ethylene midpoint.

Table IV. Intramolecular Distances (Å)

| | | | |
|---|---|---|---|
| Ti-C1 | 2.160(4) | C2-C3 | 1.404(10) |
| C1-C1′ | 1.438(5) | C2-C6 | 1.389(12) |
| C1-H1a | 0.985(20) | C3-C4 | 1.403(14) |
| Ti-C2 | 2.402(7) | C4-C5 | 1.432(15) |
| Ti-C3 | 2.353(8) | C5-C6 | 1.376(14) |
| Ti-C4 | 2.417(12) | C2-C7 | 1.478(10) |
| Ti-C5 | 2.464(10) | C3-C8 | 1.534(12) |
| Ti-C6 | 2.400(10) | C4-C9 | 1.525(16) |
| Ti-R | 2.092(5) | C5-C10 | 1.489(12) |
| Ti-E | 2.037(3) | C6-C11 | 1.501(12) |

R = $C_5Me_5$ ring centroid; E = Ethylene midpoint.

Table V. Least-Squares Plane of Cyclopentadienyl Ring

Equation[a]: $2.370 = -0.6227x + 0.7013y + 0.3470z$

| Atom | Deviation[b] | $\sigma$ |
|---|---|---|
| C2 | -0.018 | 0.007 |
| C3 | 0.009 | 0.008 |
| C4 | 0.002 | 0.012 |
| C5 | -0.014 | 0.010 |
| C6 | 0.020 | 0.010 |
| C7 | -0.215 | 0.007 |
| C8 | -0.367 | 0.007 |
| C9 | -0.225 | 0.009 |
| C10 | -0.138 | 0.011 |
| C11 | 0.017 | 0.008 |

Dihedral angle between planes defined by C1-Ti-C1′ and R-Ti-R′ is 87.8(3)° (Tilt angle, $\delta = 2.2(3)°$).

[a]Plane defined by C2 through C6.

[b]Negative values denote displacement away from Ti.

ranges found in other $(\eta\text{-}C_5Me_5)_2M$ species. Thus, the pentamethylcyclopentadienyl ring is considered to be coordinated in a normal, pentahapto manner to the titanium.

The displacements of the methyl groups out of the plane of the cyclopentadienyl ring are as much as 0.37(1) Å (Table V); these displacements, the large R-Ti-R angle, and the slight staggering of the $C_5Me_5$ rings discussed previously (torsion angle $\tau$ = 26(2)°) appear to greatly relieve the steric crowding between the $C_5Me_5$ ligands, as evidenced by the few short inter-ring C···C distances (Table VI): C7-C8′, 3.32(1); C2-C2′, 3.38(1); C2-C3′, 3.37(1) Å. In contrast, the large number of close nonbonding contacts may be cited as evidence of significant steric interaction between the ethylene and the $C_5Me_5$ ligands (Table VI): C1-C4′, 3.02(1); C1-C5, 2.95(1); C1-C5′, 3.05(1); C1-C6. 3.35(1); C1-C9′, 3.32(1); C1-C10, 3.15(1); C1-C10′, 3.36(1) Å. While all other interligand C···C contacts exceed 3.6 Å, there are also six short H···C contacts between the ethylene hydrogens and the carbons of the pentamethylcyclopentadienyl ligands (Table VI). Therefore, it is not surprising that substituted alkenes such as propene or 1-butene do not form olefin complexes analogous to 2 by reaction with $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (3).

Details of the titanium-ethylene geometry warrant further discussion since 2 represents the first isolable mono-olefin adduct of titanium. As illustrated in Figure 7, coordination of ethylene to the decamethyltitanocene fragment results in a substantial increase in the

Table VI. Intramolecular Non-Bonded Distances (Å)[a]

| | | | |
|---|---|---|---|
| C1-C4′ | 3.018(13) | Ti-H1a | 2.720(19) |
| C1-C5 | 2.949(10) | C4-H1c | 2.705(23) |
| C1-C5′ | 3.051(10) | C5-H1a | 2.628(21) |
| C1-C6 | 3.350(10) | C5-H1c | 2.805(21) |
| C1-C9′ | 3.322(11) | C9-H1c | 2.688(22) |
| C1-C10 | 3.150(8) | C10-H1a | 2.444(20) |
| C1-C10′ | 3.365(8) | C10-H1c | 2.857(20) |
| C2-C2′ | 3.377(10) | | |
| C2-C3′ | 3.372(10) | | |
| C2-C8′ | 3.320(12) | | |

[a]Listed are all distances less than 3.60 Å for C-C and 3.00 Å for C-H, excluding methyl hydrogens.

carbon-carbon bond length, from 1.337(2) Å for free ethylene[24] to 1.438(5) Å for 2 (C1-C1', Table IV). This distance is significantly greater than that found for Zeise's salt (1.375(4) Å)[25] and for many other olefin complexes (C-C, Table VII) but is in good agreement with the C-C bond distances found for ethylene adducts of low valent, electron-rich metal centers (e.g., 1.406(13) Å for $(\eta\text{-}C_5H_5)_2Nb(C_2H_5)(\eta\text{-}C_2H_4)$,[26] 1.434(13) Å for $(PPh_3)_2Pt(\eta\text{-}C_2H_4)$,[27] 1.477(4) Å for $(\eta\text{-}C_5Me_5)Ta(CHCMe_3)(\eta\text{-}C_2H_4)(PMe_3)$;[28] Table VII). Displacement of the hydrogen atoms from the planar ethylene geometry is also observed. Following the convention of Stalick and Ibers,[29] the "bending" of the hydrogens away from the metal can be measured as the angle ($\alpha$) between the normals of the C-H-H planes (Figure 7); the large $\alpha$ angle found for 2, 70(4)°, is comparable to those found for electron-rich metal ethylene compounds (Table VII). Other bond distances and angles for 2 are given in Tables III and IV.

The large $\alpha$ value and significant lengthening of the ethylene C-C bond observed for 2 and for other electron-rich metal olefin compounds are considered indicative of substantial electron back donation from the metal to the ethylene.[30] Back donation in 2 can occur through overlap of the $b_2$ orbital of the metallocene with the ethylene $\pi^*$ orbital as shown in Figure 8, and impart the formally Ti(II) $\pi$-olefin complex with partial Ti(IV) metallacyclopropane character. Based on comparisons with other structural data, the structure of 2 would appear to be intermediate along the continuum between the Ti(II) ethylene and Ti(IV) metallacyclopropane limiting structures.[30]

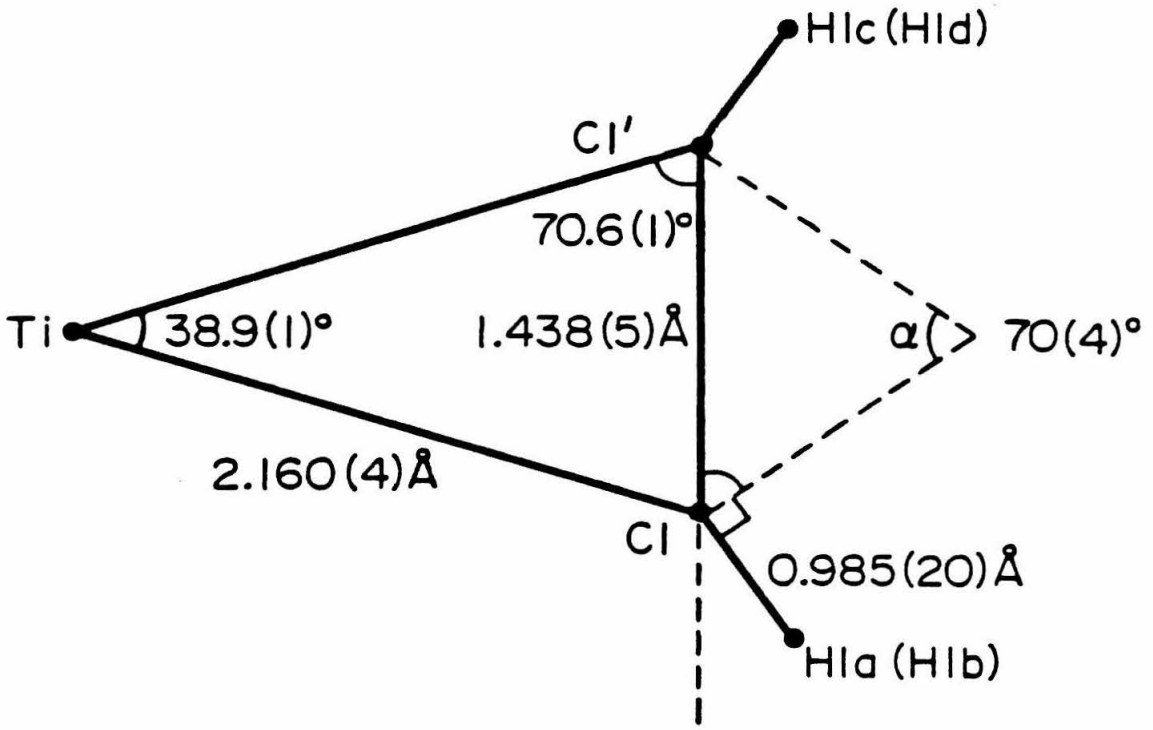



Figure 7.

Table VII. Structural Data for Selected Ethylene and Heterocyclopropane Compounds

| Compound | C-C (Å) | C-H (Å) | $\alpha$ (deg) | Method | Ref. |
|---|---|---|---|---|---|
| $C_2H_4$ | 1.337(2) | 1.103(2) | 0 | a | 24 |
| $(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2F_4)(\eta\text{-}C_2H_4)$ | 1.358(9) | 0.956(40) | 42.4 | b | 33a |
| $(\eta\text{-}C_5H_5)Rh(SO_2)(\eta\text{-}C_2H_4)$ | 1.366(5) | 0.95(10) | - | b | 33b |
| $KCl_3Pt(\eta\text{-}C_2H_4)\cdot H_2O$ | 1.375(4) | 1.087(7) | 32.5 | c | 25 |
| $(PMe_2Ph)_2RuCl_2(CO)(\eta\text{-}C_2H_4)$ | 1.376(10) | 0.92(18) | 24(11) | b | 33c |
| $(\eta\text{-}C_5H_5)_2Nb(C_2H_5)(\eta\text{-}C_2H_4)$ | 1.406(13) | 0.98(14) | 52.5 | b | 26 |
| $(\eta\text{-}C_5H_5)Rh(PPh_3)(\eta\text{-}C_2H_4)$ | 1.408(16) | 0.90(5) | 38,58 | b | 33d |
| $(PPh_3)_2Ni(\eta\text{-}C_2H_4)$ | 1.431(15) | -- | - | b | 33e |
| $(PPh_3)_2Pt(\eta\text{-}C_2H_4)$ | 1.434(13) | -- | - | b | 27 |
| $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ | 1.438(5) | 0.985(20) | 70(4) | b | this work |
| $[(o\text{-}CH_3C_6H_4O)_3P]_2Ni(\eta\text{-}C_2H_4)$ | 1.46(2) | -- | - | b | 33f |
| $(\eta\text{-}C_5Me_5)Ta(CHCMe_3)(PMe_3)(\eta\text{-}C_2H_4)$ | 1.477(4) | 1.090(8) | 68.5 | c | 28 |
| $\overline{C_2H_4S}$ | 1.484(3) | 1.083(2) | 57.1 | d | 33g |
| $\overline{C_2H_4PH}$ | 1.502(5) | 1.093(5) | 61.0 | d | 33h |

[a]Electron diffraction. [b]X-ray diffraction. [c]Neutron diffraction. [d]Microwave spectroscopy.

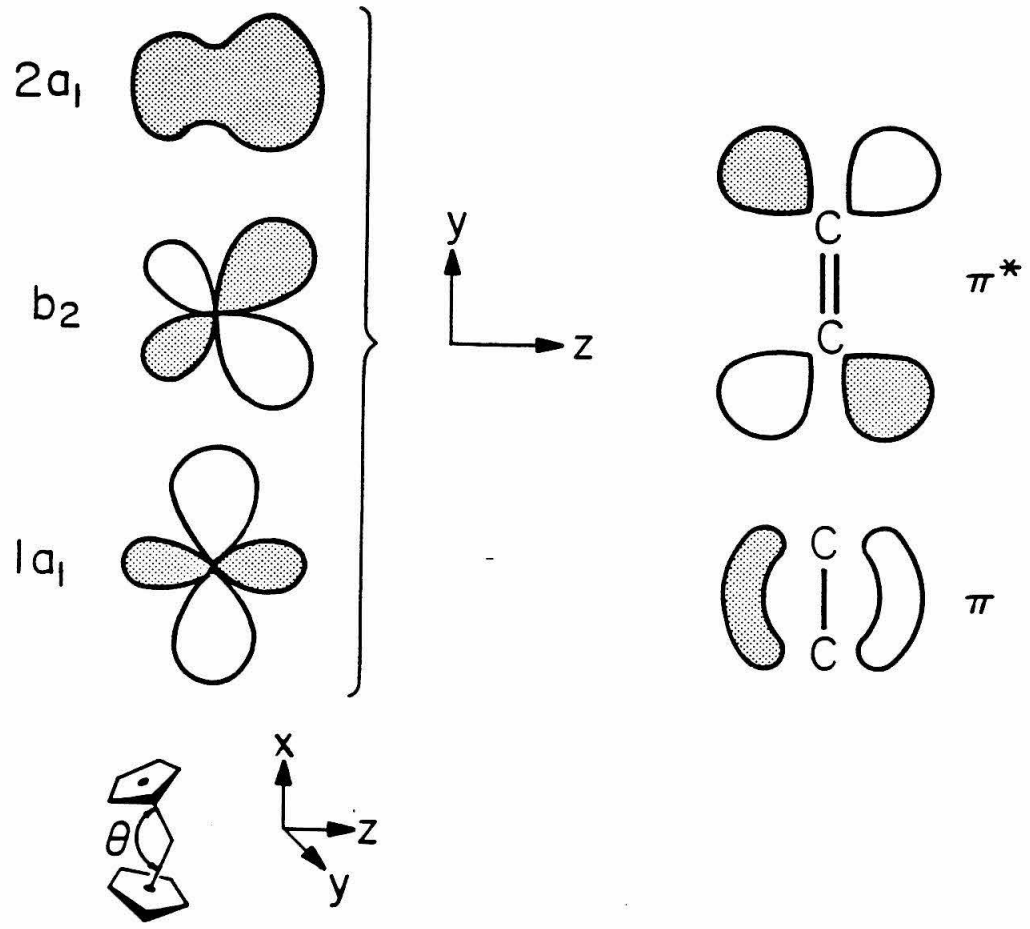



Figure 8. Frontier orbitals of the bent metallocene fragment and $\pi$ orbitals of the ethylene molecule.

General Reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$. The titanium ethylene complex undergoes facile reactions with a variety of substrates, consistent with its formulation as a coordinatively unsaturated $\pi$-olefin species. Toluene solutions of 2 react with carbon monoxide above -78° to produce ethylene (1.0 mol/mol 2) and the dicarbonyl compound, $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$ (4).[14a] Similarly, treatment with methyl isocyanide

$$(C_5Me_5)_2Ti(C_2H_4) + 2CO \rightarrow (C_5Me_5)_2Ti(CO)_2 + C_2H_4 \qquad (3)$$

(eq. 4), results in quantitative displacement of $C_2H_4$. The resulting isocyanide compound, $(\eta\text{-}C_5Me_5)_2Ti(CNMe)_2$ (5) has been characterized only in solution by $^1H$ and $^{13}C$ NMR, since it is found to be unstable above 0°. The mild conditions under which these reactions occur are

$$(C_5Me_5)_2Ti(C_2H_4) + 2CNMe \rightarrow (C_5Me_5)_2Ti(CNMe)_2 + C_2H_4 \qquad (4)$$

suggestive of an associative substitution pathway[31] as outlined in eq. 5. Both CO and MeNC are sterically unhindered and good $\pi$-acceptor ligands; thus, the addition of L(CO, MeNC) to the titanium ethylene

$$2 \underset{-L}{\overset{+L}{\rightleftharpoons}} \left[Cp^*_2Ti\begin{smallmatrix}\swarrow L\\ \searrow \;/\!/\end{smallmatrix}\right] \underset{+C_2H_4}{\overset{-C_2H_4}{\rightleftharpoons}} \left[Cp_2{}^*Ti \leftarrow L\right] \underset{-L}{\overset{+L}{\rightleftharpoons}} Cp_2{}^*TiL_2 \qquad (5)$$

C D

complex would be expected to labilize the ethylene and lead, perhaps via C and D, to $Cp^*_2TiL_2$ ($Cp^* = \eta\text{-}C_5Me_5$).

The ligand substitution chemistry of 2 may be contrasted with the behavior of the alkyl and aryl derivatives of Ti(III), Ti(IV), and Zr(IV);

these coordinatively unsaturated compounds undergo rapid migratory insertion reactions with carbon monoxide and alkyl or aryl isocyanides, forming acyl and iminoacyl complexes or products derived therefrom.[32] The reactivity of 2 with dihydrogen also differs qualitatively from the hydrogenolyses of dialkyl compounds of Ti(IV) and Zr(IV), such as $(\eta\text{-}C_5Me_5)_2TiMe_2$ (6). The latter species, formally a $d^0$ complex incapable of oxidative addition at the metal center, does not react with $H_2$ prior to its decomposition, even at elevated pressures.[14a] The hydrogenation of 2 to $(\eta\text{-}C_5Me_5)_2TiH_2$ (7), however, proceeds smoothly

$$(C_5Me_5)_2Ti(C_2H_4) + 2H_2 \rightarrow (C_5Me_5)_2TiH_2 + C_2H_6 \qquad (6)$$

at -50° in aromatic solvents according to eq. 7 and is likened to the rapid hydrogenations of $(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)TiCH_3$[14a] and $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}MeC{\equiv}CMe)$.[35] The striking differences in the reactivity of 2 with hydrogen (vis-a-vis 6) are attributed to the facile formation of the eighteen-electron Ti(IV) intermediate, $(\eta\text{-}C_5Me_5)_2TiH_2(\eta\text{-}C_2H_4)$.

A number of other reactions have been used to characterize $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$. Treatment of 2 at -78° with two equivalents of anhydrous HCl results in the immediate liberation of ethane (1.0 mol/mol 2) and generation of the dichloride 1. When 1.0 mol HCl/

$$(C_5Me_5)_2Ti(C_2H_4) + 2\ HCl \longrightarrow (C_5Me_5)_2TiCl_2 + C_2H_6 \qquad (7)$$

mol 2 is employed, a small concentration of an ethyltitanium species is observed (NMR) in addition to the expected $C_2H_6$, 1, and unreacted 2.[36] Excess methyl iodide slowly reacts with 2 at elevated temperatures (ca. 90 min at 80°), releasing ethylene (0.92 mol/mol 2) and

forming $(\eta\text{-}C_5Me_5)_2TiI(Me)$ (8) (ca. 90%) with small amounts of other

$$(C_5Me_5)_2Ti(C_2H_4) + CH_3I \rightarrow C_2H_4 + (C_5Me_5)_2TiI(Me) + \underset{\sim}{6} \qquad (8)$$

$(\eta\text{-}C_5Me_5)_2Ti$ derivatives, predominantly 6 (by $^1H$ NMR). A sluggish reaction also occurs between the titanium ethylene complex and the dichloride 1, as shown in eq. 9. Upon heating at 80° for about one hour, benzene and toluene solutions of 1 and 2 (1:1) produce

$$(C_5Me_5)_2Ti(C_2H_4) + (C_5Me_5)_2TiCl_2 \rightarrow 2(C_5Me_5)_2TiCl + C_2H_4 \qquad (9)$$

ethylene and the deep blue paramagnetic compound, $(\eta\text{-}C_5Me_5)_2TiCl$ (9).[16] Between -78° and +80°, the formation of adducts such as $(\eta\text{-}C_5Me_5)_2TiCl(\eta\text{-}C_2H_4)$ and $[(\eta\text{-}C_5Me_5)_2TiCl]_2(\mu\text{-}C_2H_4)$ is not observed upon exposure of toluene solutions of 9 to added ethylene ($\leq$ 1 atm).

Reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with Olefins. As shown in eq. 10, ethylene reacts reversibly with 2 in aromatic solvents to yield an equilibrium mixture containing $(\eta\text{-}C_5Me_5)_2\overbrace{TiCH_2(CH_2)_2CH_2}$ (10), a

$$(C_5Me_5)_2Ti(C_2H_4) + C_2H_4 \rightleftharpoons (C_5Me_5)_2Ti\langle\ \rangle \qquad (10)$$

compound previously noted by Whitesides as the product of the reaction between $(\eta\text{-}C_5Me_5)_2TiCl_2$ (1) and 1,4-dilithiobutane.[32d] The addition of higher olefins ($C_2H_3R$) to 2 does not result in the formation of metallacyclopentanes, presumably due to unfavorable steric interactions

$$(C_5Me_5)_2Ti(C_2H_4) + C_2H_3R \not\rightarrow (C_5Me_5)_2Ti\langle\ \rangle^{R} \quad R = Me, Et, etc. \qquad (11)$$

between the alkyl substituent and the bulky $C_5Me_5$ ligands (eq. 11).

The formation of 10 from 2 is an example of the oxidative coupling of alkenes by an electron-rich metal center to give a metallacyclopentane, a reaction which has been observed with other low valent titanium, zirconium, niobium, and tantalum complexes.[9,10,32,37]

$$0.6\,(C_5Me_5)_2Ti(C_2H_4) + 0.4\,(C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2} + 2HCl$$

$$\rightarrow (C_5Me_5)_2TiCl_2 + 0.6\,C_2H_6 + 0.4\,C_4H_{10} \qquad (12)$$

Red-orange 10 is not sufficiently insoluble or stable to loss of $C_2H_4$ under vacuum to allow isolation and separation from 2; however, it has been characterized in solution as a monomeric Ti(IV) metallacyclopentane complex by $^1H$ and $^{13}C$ NMR spectroscopy, chemical degradation (eq. 12), and equilibria studies (Figs. 1 and 9). The degradation products and the spectroscopic data are quite similar to those of the Zr(IV) compound, $(\eta\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$,[32e] and rule out the formulation of 10 as the Ti(II) bis($\pi$-olefin) complex, $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)_2$ (E). Such a species is suggested, however, as an intermediate in the reaction of 2 with ethylene (eq. 13).

$$(C_5Me_5)_2Ti(C_2H_4) + C_2H_4 \rightleftharpoons [(C_5Me_5)_2Ti(\underset{E}{\;\;}\!\!=\!\!=) \;] \rightleftharpoons (C_5Me_5)_2Ti\langle\!\rangle \qquad (13)$$

Carbonylation (< 5 atm) of solutions containing 2, 10, and $C_2H_4$ results in the quantitative formation of 4 (NMR); moreover, no organic products besides ethylene are detected (NMR, IR), consistent with the

$$\begin{matrix}(C_5Me_5)_2Ti(C_2H_4)\\ +\\ (C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}\end{matrix} \xrightarrow[0\text{-}70^\circ]{CO} (C_5Me_5)_2Ti(CO)_2 + C_2H_4 \qquad (14)$$

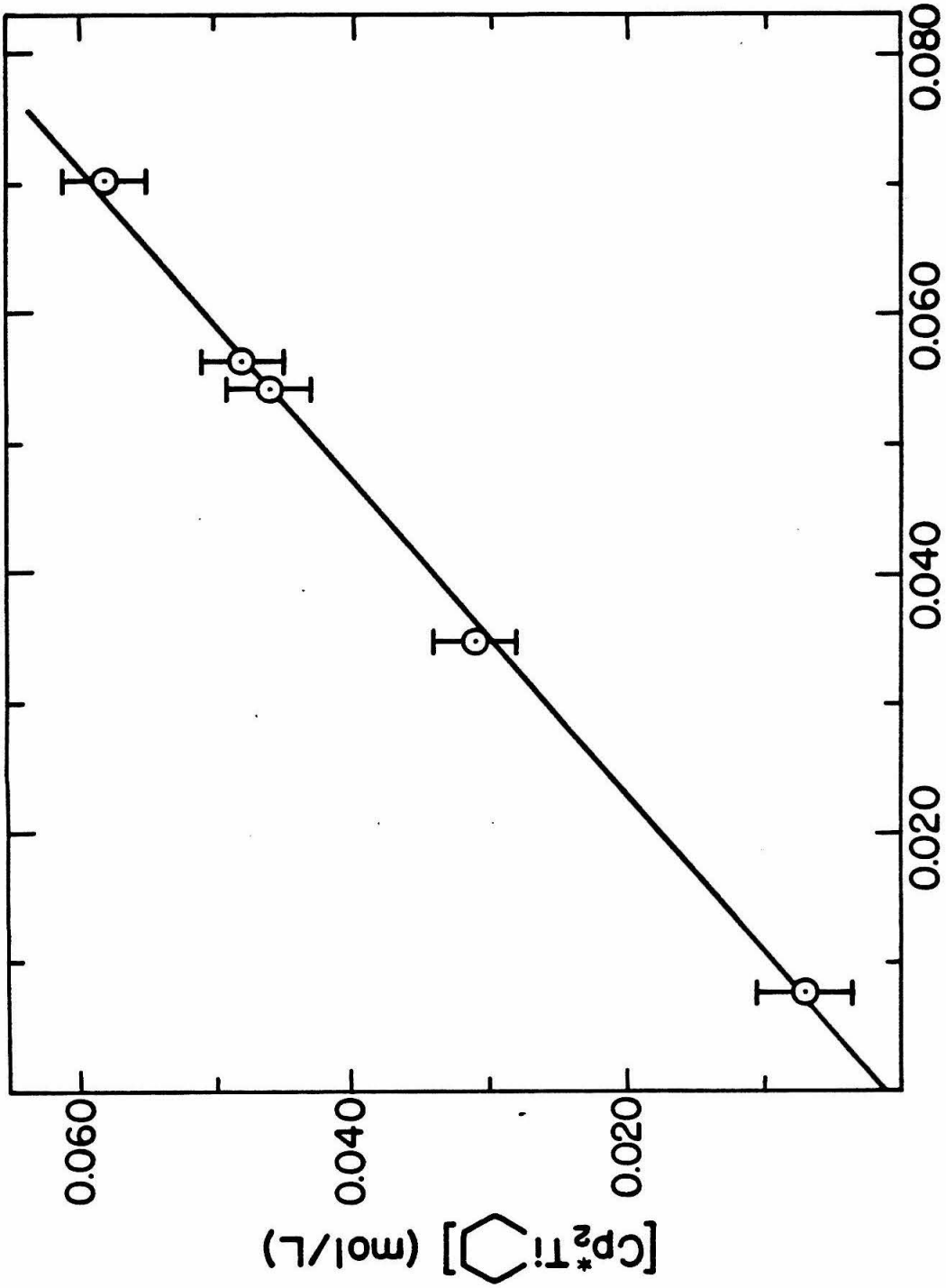



Figure 9. Equilibrium measurement of $2 + C_2H_4 \rightleftharpoons 10$ at 34°.

results previously reported for $\underset{\sim}{10}$ + CO.[32d]

Interestingly, benzene and toluene solutions containing $\underset{\wedge}{2}$ and $\underset{\sim}{10}$ are active in catalyzing the conversion of ethylene specifically to 1,3-butadiene and ethane under very mild conditions (25°, ≤ 4 atm).[38]

$$3C_2H_4 \xrightarrow[25^\circ]{[\underset{\wedge}{2} + \underset{\sim}{10}]} CH_2{=}CH{-}CH{=}CH_2 + C_2H_6 \qquad (15)$$

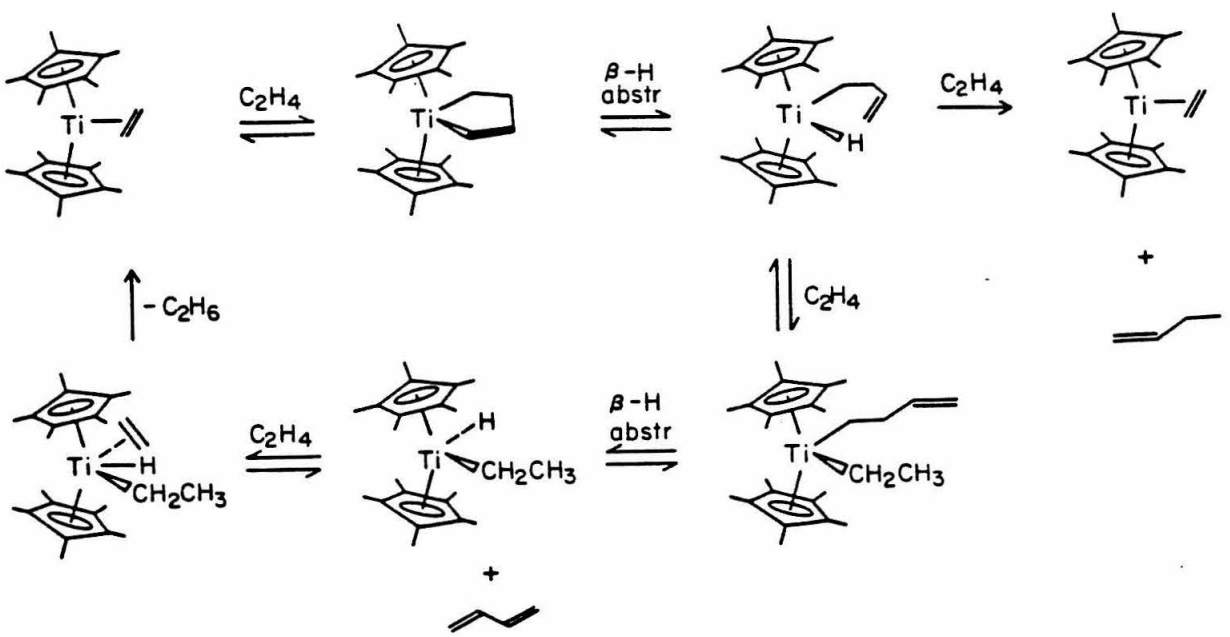
Doubly labelled butadiene and ethane are produced in addition to the unlabelled materials when a 9:1 mixture of normal and $^{13}C$ enriched (90% $^{13}C_2$) ethylene is added to $\underset{\wedge}{2}$, thus confirming that the butadiene and ethane are derived from ethylene. While traces of polyethylene are found (< 2 mg, identified by IR), no butane or butenes are detected and no decomposition of $\underset{\wedge}{2}$ is observed after one year (NMR).

Investigation of the reaction shown above has been severely hampered by an exceedingly slow rate of conversion: at the ethylene pressures which are accessible (≤ 5 atm), the rate is ca. 1-2 turnovers · $yr^{-1}$ at 25° based on the total concentration of titanium species, $[\underset{\wedge}{2} + \underset{\sim}{10}]$. The limited data which are available suggest that the observed rate of reaction is enhanced by increased ethylene concentrations. In another experiment, 1-butene is found to be stable under the reaction conditions; even after six months, the concentration of added 1-butene is unchanged[39] while the formation of butadiene and ethane is similarly unaffected.

These results argue against the specific formation of butadiene being due to the presence of an alkene disproportionation catalyst;[40] moreover, they demonstrate the preferential involvement of $C_2H_4$,

rather than 1-butene or 1,3-butadiene, as the hydrogen-accepting substrate. Similar ethylene selectivity is observed for 2 (eq. 11) and suggests the intermediacy of 10 in the reaction (eq. 15). Recognizing that the product of $\beta$-hydrogen abstraction from 10 is an alkyl hydride complex of titanium which, based on the reactivity of related zirconium and tantalum systems,[41] may undergo ethylene addition faster than reductive elimination, a possible mechanism for the formation of butadiene and ethane is outlined in Scheme 1. The formation of a small amount of butadiene when the thermolysis of $(\eta\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$ is performed in the presence of ethylene (but not when it is carried out under vacuum) may be similarly explained.[10b]

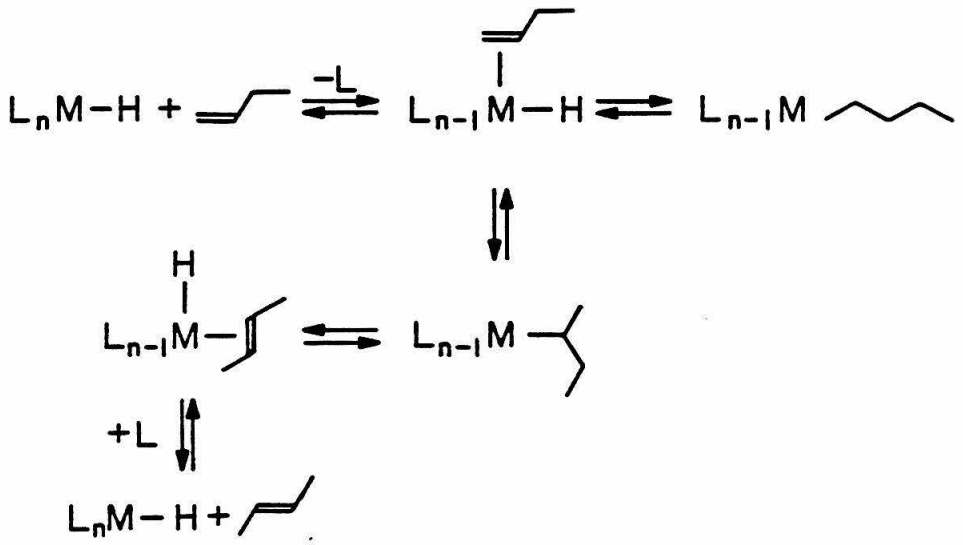
Scheme 1



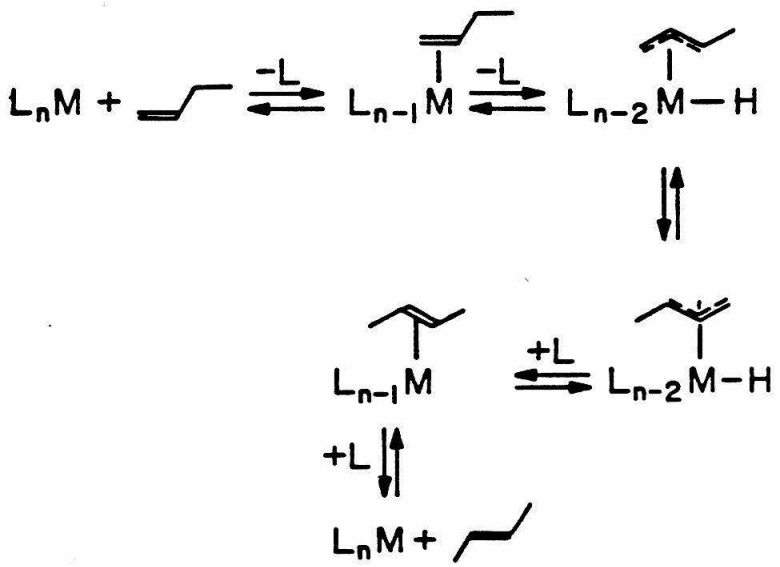
As mentioned earlier, the addition of propene, 1-butene, and 1-hexene to $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (3) does not result in the formation of the alkene analogues of the titanium ethylene adduct (2), nor does displacement of ethylene, alkene oligomerization, or formation of metallacyclopentanes occur. Both 2 and 3, however, catalyze the isomerization of 1-butene and 1-hexene to primarily trans-2-butene and trans-2-hexene, respectively.[42] The isomerization of 1-butene by 2 has been investigated and found to exhibit a first-order dependence on [2] and [1-butene] with an energy of activation ($E_a$) of 23.8 $\pm$ 1.4 kcal $\cdot$ mol$^{-1}$. The rate of isomerization is inhibited by added ethylene; as shown in Fig. 2, the isomerization of 1-butene at 106° varies linearly with $[C_2H_4]^{-1}$ for ethylene concentrations between 0.025 and 0.277 M and gives within experimental error an intercept ($[C_2H_4]^{-1} = 0$) of zero. Since the concentration of $(\eta\text{-}C_5Me_5)_2\overline{Ti}CH_2(CH_2)_2\overline{C}H_2$ (10) is negligible under these conditions (Fig. 1), the inverse $[C_2H_4]$ dependence for the reaction is consistent with an ethylene-free titanium species as the catalytically active component.

Transition metal catalyzed isomerization of alkenes has been discussed by Casey and Cyr.[43] The commonly observed pathway involves the addition of an alkene to an often undetected metal hydride species, generating a metal alkyl intermediate (Scheme 2), while an alternative mechanism -- coordination of an alkene to a metal center, followed by activation of an allylic C-H bond to produce an allyl hydride intermediate (Scheme 3) -- has been clearly established in only one instance.[43] Since the addition of linear alkenes to

Scheme 2




Scheme 3



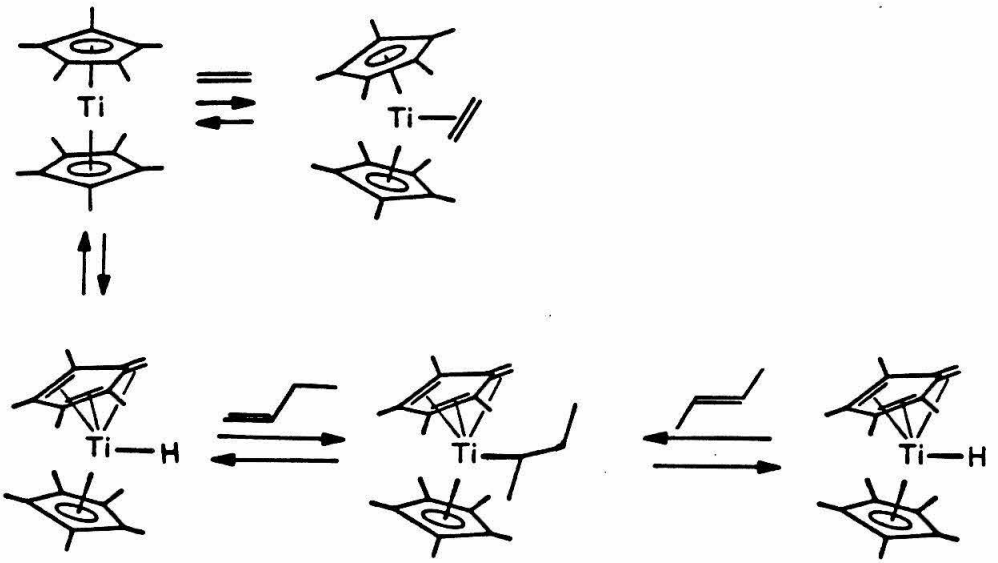
$[(\eta\text{-}C_5Me_5)_2ZrN_2]_2(\mu\text{-}N_2)$ affords isolable allyl hydride derivatives of $(\eta\text{-}C_5Me_5)_2Zr$, the analogous $(\eta\text{-}C_5Me_5)_2TiH(allyl)$ species were considered viable intermediates for the isomerization of 1-butene and 1-hexene by $\underset{\sim}{2}$. The two mechanisms may be distinguished by isomerization of a mixture of perdeuterio and perprotio alkene: if the isomerization is hydride mediated, H-D scrambling among the alkene molecules will be observed, whereas no H-D scrambling should be detected if an allyl hydride mechanism obtains. Propene-$d_0$ and propene-$d_6$ (2 : 1), heated in a benzene solution of $\underset{\sim}{2}$ at 71°, is found to have undergone extensive H-D scrambling after 4 hrs, as measured by $^2H$ NMR (eq. 16). The appearance of resonances at $\delta$ 1.67 and 2.05 in the $^2H$ NMR spectrum establishes the presence of deuterated $\underset{\sim}{2}$. Thus, the

$$C_3H_6 + C_3D_6 \xrightarrow{[\underset{\sim}{2}]} C_3H_xD_{6-x} \qquad 0 \leq x \leq 6 \tag{16}$$

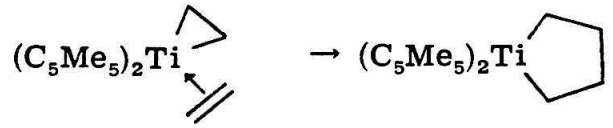
isomerization of alkenes by $\underset{\sim}{2}$ proceeds via a metal hydride intermediate. A likely species consistent with the kinetic data is a hydride tautomer of $(\eta\text{-}C_5Me_5)_2Ti$, $(\eta\text{-}C_5Me_5)(\eta\text{-}C_5Me_4CH_2)TiH$ ($\underset{\sim}{11}$), a compound observed previously in equilibrium with $(\eta\text{-}C_5Me_5)_2Ti$.[14b] An isomerization mechanism involving $\underset{\sim}{11}$ is outlined in Scheme 4.

Structure and reactivity patterns characterize $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ as an electron-rich Ti(II) $\pi$-olefin complex. The presence of the bulky $C_5Me_5$ rings provide a limited stability range for $\underset{\sim}{2}$. Its chemistry is dominated by loss of ethylene from the metal center, either as ethylene or ethane. Thus, $\underset{\sim}{2}$ is a convenient source of the $(\eta\text{-}C_5Me_5)_2Ti$ fragment, the behavior of which is well documented.[14b]

Scheme 4




Beyond establishing the titanium $\pi$-olefin adduct as a stable entity, the chemistry of $\underset{\sim}{2}$ appears to bear little resemblance to olefin polymerization processes. Although formation of the metallacyclopentane from the ethylene complex might be considered a formal migratory insertion reaction involving the eighteen-electron, Ti(IV) metallacyclopropane $\pi$-olefin compound, $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2CH_2}(\eta\text{-}C_2H_4)$ (eq. 17), the products formed by the addition of CO and $CNCH_3$ to $\underset{\sim}{2}$ argue against




(17)

such a description. The formation of the metallacyclopentane does demonstrate that $\underset{\sim}{2}$ is capable of reactivity which retains the ethylene in the titanium product. Moreover, the butadiene-ethane (and butene) production, of minor importance in its own right, suggests that

subsequent reactions are possible which do not involve simple ethylene dissociation. The interactions of $\underset{\sim}{2}$ with other unsaturated organic substrates which utilize and more fully explore its reactivity are reported in Chapter 2.

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# Chapter II

## Reactivity of Unsaturated Organic Compounds With Bis Pentamethylcyclopentadienyl Ethylene Titanium (II)

## Introduction

A predominant feature of the reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ (1) with CO, CNR, $H_2$ or HCl is the ease with which the ethylene ligand is lost.[1] This is used to full advantage in the isomerization of alkenes, since a ready source of $(\eta\text{-}C_5Me_5)_2Ti$ or its tautomer $(\eta\text{-}C_5Me_5)(\eta\text{-}C_5Me_4CH_2)TiH$ is highly desirable. However, the ready dissociation of ethylene from 1 would appear to preclude the incorporation of ethylene into the reaction products.

The exception to the rapid loss of ethylene from 1 is the formation of the metallacyclopentane species, $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$, which is the coupling product of 1 and a second equivalent of ethylene. The belief that the sterically large $C_5Me_5$ ligands tend to destabilize products which incorporate ethylene suggested that reactions of 1 with very small substrate molecules, particularly those which also contain relatively weak bonds, might lead to associative reactivity. Based on the slow production of butadiene and ethane observed,[1] these coupling products could themselves be capable of subsequent chemistry. Therefore, the investigation of the reactivity of 1 with nitriles, alkynes, and (briefly) oxygenates was undertaken, the results of which are described below.

## Results

Reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with Nitriles. Addition of 1.02 equivalents of $CH_3CN$ to a toluene solution of $\underset{\sim}{1}$ below -50° results in the quantitative formation of the metallacycloimine complex, $(\eta\text{-}C_5Me_5)_2\overline{TiN=C(CH_3)CH_2CH_2}$ ($\underset{\sim}{2}$). Red orange $\underset{\sim}{2}$ has been characterized by $^1H$ and $^{13}C$ NMR (Tables I and II) as well as infrared spectroscopy ($\nu_{CN}$ = 1638 $cm^{-1}$). Above -10°, an equilibrium is established between $\underset{\sim}{2}$ and its metallacycloenamine tautomer,

$$(C_5Me_5)_2Ti(C_2H_4) + CH_3CN \rightarrow (C_5Me_5)_2Ti\langle \text{N} \rangle \qquad (1)$$

$\underset{\sim}{1}$ $\qquad\qquad$ $\underset{\sim}{2}$

$$(C_5Me_5)_2Ti\langle \text{N} \rangle \rightleftharpoons (C_5Me_5)_2Ti\langle \text{HN} \rangle \qquad (2)$$

$\underset{\sim}{2}$ $\qquad\qquad$ $\underset{\sim}{3}$

$(\eta\text{-}C_5Me_5)_2\overline{TiNHC(CH_3)=CHCH_2}$ ($\underset{\sim}{3}$); the equilibrium constant, $K_{eq}([\underset{\sim}{3}]/[\underset{\sim}{2}])$, varies from 0.4 at 0° to 0.8 at 25°. Isomerization of $(\eta\text{-}C_5Me_5)_2\overline{TiN=C(CD_3)CH_2CH_2}$ ($\underset{\sim}{2}\text{-}\underline{d}_3$), prepared from $\underset{\sim}{1}$ and $CD_3CN$, yields only $(\eta\text{-}C_5Me_5)_2\overline{TiNHC(CD_3)=CHCH_2}$ ($\underset{\sim}{3}\text{-}\underline{d}_3$). No H-D scrambling

$$(C_5Me_5)_2Ti\langle \text{N}\!-\!CD_3 \rangle \rightleftharpoons (C_5Me_5)_2Ti\langle \text{HN}\!-\!CD_3 \rangle \qquad (3)$$

$\underset{\sim}{2}\text{-}\underline{d}_3$ $\qquad\qquad$ $\underset{\sim}{3}\text{-}\underline{d}_3$

is observed after two days at 25° ($^2H$ NMR).

Carbon-carbon bond formation between the nitrile and the ethylene groups in $\underset{\sim}{2}$, which is substantiated by the observed $^{13}C$-$^{13}C$

Table I. Proton NMR Data

| Compound; solvent and temperature* | | Assignment | Chemical Shift | Multiplicity | $J_{H-H}$ |
|---|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiN=C(CH_3)CH_2CH_2}$ | 2 | a | 1.82 | s | |
| a d c b | | b | 0.63 | t | 7.0 |
| | | c | 3.33 | t | 7.0 |
| ($C_7D_8$, 0°) | | d | 1.57 | s | |
| $(C_5Me_5)_2\overline{TiNHC(CH_3)=CHCH_2}$ | 3 | a | 1.72 | s | |
| a d e c b | | b | (not observed) | | |
| | | c | 5.03 | t | 6 |
| ($C_7D_8$, 0°) | | d | 6.19 | s | 72** |
| | | e | 1.81(observed in $^2H$ spectrum) | | |
| $(C_5Me_5)_2\overline{TiN=C(CH_2CH_3)CH_2CH_2}$ | 4 | a | 1.83 | s | |
| a d e c b | | b | 0.68 | t | 7.3 |
| | | c | 3.32 | t | 7.3 |
| ($C_6D_6$) | | d | 1.12 | q | 7.0 |
| | | e | 0.92 | t | 7.0 |

Table I. (continued)

| | | | | |
|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiN=C(CMe_3)CH_2CH_2}$ 5 | a | 1.80 | s | |
| a d c b | b | 0.48 | t | 7.1 |
| | c | 3.43 | t | 7.1 |
| $(C_7D_8)$ | d | 1.01 | s | |
| $(C_5Me_5)_2\overline{TiN=C(C_6H_4CH_3)CH_2CH_2}$ 6 | a | 1.83 | s | |
| a e,f d c b | b | 0.68 | t | 7.1 |
| | c | 3.88 | t | 7.1 |
| $(C_7D_8)$ | d | 2.11 | s | |
| | e | 6.91 | d | 8.3 |
| | f | 7.38 | d | 8.3 |
| $(C_5Me_5)_2\overline{TiNHC(CH_2CH_3)=CHCH_2}$ 7 | a | 1.73 | s | |
| a d e f c b | b | (not observed) | | |
| | c | 5.12 | t | 4 |
| $(C_6D_6)$ | d | 6.43 | s | |
| | e | 2.13 | q | 7 |
| | f | (not observed) | | |

Table I (continued)

| | | | | | |
|---|---|---|---|---|---|
| $(C_5Me_5)\overline{TiCH=C(CH_3)CH_2CH_2}$ | 8 | a | 1.76 | s | |
| a d e c b | | b | 0.83 | t | 7.5 |
| | | c | 2.21 | t (br) | 7.5 |
| $(C_6D_6)$ | | d | 4.90 | q | 1.0 |
| | | e | 1.60 | dt | 1.0,1.0 |
| $(C_5Me_5)_2Ti(CH_2CH_3)(C\equiv CCH_3)$ | 9 | a | 1.90 | s | |
| | | b | 0.57 | q | 7.5 |
| | | c | 1.15 | t | 7.5 |
| $(C_6D_6)$ | | d | 1.68 | s | |
| $(C_5Me_5)_2Ti[C\equiv CC(CH_3)_3](CH_2CH_3)$ | 10 | a | 1.88 | s | |
| a d b c | | b | 0.41 | q | 7.0 |
| $(C_6D_6)$ | | c | (not observed) | | |
| | | d | 1.23 | s | |
| $(C_5Me_5)_2Ti[C\equiv CC(CH_3)_3](CH_3)$ | 11 | a | 1.87 | s | |
| a c b | | b | -0.15 | s | |
| $(C_6D_6)$ | | c | 1.24 | s | |

Table I (continued)

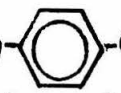
| | | | | |
|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(CH_3)CH_2CH_2}$ 12 | a | 1.80 | s | |
| a d e c b | b | 1.06 | t | 7.4 |
| | c | 2.13 | t (br) | 7.4 |
| $(C_6D_6)$ | d | 1.03 | tq | 0.9, 0.9 |
| | e | 1.43 | q | 0.9 |
| $(C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CCH_3)$ 13 | a | 1.89 | s | |
| a b | b | 1.74 | s | |
| $(C_7D_8)$ | | | | |
| $(C_5Me_5)_2Ti(\eta$-  $\text{-}C{\equiv}CC_6H_5)$ 14 | a | 1.74 | s | |
| a b c d | b | 6.80 | m | |
| $(C_6D_{12})$ | c | 6.54 | d | 8.0 |
| | d | 6.86 | d | 8.0 |
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(CH_2CH_3)CH_2CH_2}$ 18α | a | 1.78 | s | |
| a b e f c d | b | 1.00 | s (br) | |
| $(C_6D_6)$ | c | | | |
| | d | 0.9-2.1 | m | |
| | e | | | |
| | f | | | |

Table I (continued)

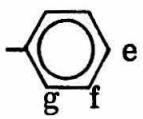
| | | | | |
|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(C_5H_{11})CH_2CH_2}$ 19α | a | 1.83 | s | |
| a d e-i c b | b-i | 0.8-2.1 | m | |
| $(C_7D_8)$ | | | | |
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(C_6H_5)CH_2CH_2}$ 20α | a | 1.81 | s | |
| a d e,f,g c b | b | 1.12 | t | 7.9 |
|  | c | 2.52 | tq | 7.9, 2.0 |
| | d | 1.04 | t | 2.0 |
| $(C_6D_6)$ | e | 7.00-7.15 | m | |
| | f | 7.25 | s | |
| | g | 7.30 | m | |
| $C_5Me_5)_2\overline{TiOC(O)CH_2CH_2}$ 22 | a | 1.67 | s | |
| a c b | b | 1.09 | t | 8.0 |
| $(C_7D_8)$ | c | 3.24 | t | 8.0 |

Table I (continued)

| | | | | |
|---|---|---|---|---|
| $(C_5Me_5)(C_5Me_5)\overline{TiOCH(CH_3)CHH'CHH'}$ 23 | a | 1.85 | s | |
| a b c d e f g h | b | 1.82 | s | |
| | c | 4.71 | dqd | 11.0, 6.1, 3.7 |
| $(C_7D_8)$ | d | 0.95 | d | 6.1 |
| | e | 2.67 | dddd | 12.2, 12.2, 11.0, 7.3 |
| | f | 2.43 | dddd | 12.2, 7.3, 3.7, 1.2 |
| H′ cis to methine H | g | 0.23 | ddd | 11.0, 7.3, 1.2 |
| | h | 2.17 | ddd | 12.2, 11.0, 7.3 |



* Sample temperature 34° unless given.

** $^1J_{^{15}N\text{-}H}$

Table II. $^{13}C$ NMR Data.

| Compound: solvent and temperature* | | Assignment | Chemical Shift | $^{1}J_{C-H}$ (m) | $^{1}J_{C-C}$ | $^{x}J_{C-H}$ |
|---|---|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiN=C(CH_3)CH_2CH_2}$ | 2 | a | 119.5 | (s) | | |
| a b e f d c | | b | 11.9 | 126 (q) | | |
| $(C_7D_8$, -30°) | | c | 44.0 | 124 (t) | 33 (cd) | 3 (cf)‡ |
| | | d | 59.2 | 120 (t) | 40 (de) | 15 (df)‡ |
| | | e | 164.2 | (s) | 42 (ef) | |
| | | f | 26.3 | 125 (q) | | |
| $(C_5Me_5)_2\overline{TiNHC(CH_3)=CHCH_2}$ | 3 | a | 117.0 | (s) | | |
| a b e f d c | | b | 12.0 | 126 (q) | | |
| $(C_7D_8)$ | | c | 61.4 | 132 (t) | 37 (cd) | 5 (cf)‡ |
| | | d | 114.1 | 154 (d) | | 8 (df)‡ |
| | | e | 148.3 | (s) | | |
| | | f | 24.6 | 125 (q) | | |
| $(C_5Me_5)_2\overline{TiN=C(CH_2CH_3)CH_2CH_2}$ | 4 | a | 119.6 | (s) | | |
| a b e f g d c | | b | 11.9 | 126 (q) | | |
| $(C_7D_8)$ | | c | 44.2 | 125 (t) | 33 (cd) | |
| | | d | 57.9 | 119 (t) | | |
| | | e | 169.0 | (s) | | |

Table II. (continued)

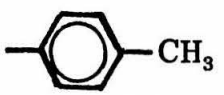
| | | | | |
|---|---|---|---|---|
| | f | 31.5 | 121 (t) | |
| | g | 10.9 | 123 (q) | |
| $(C_5Me_5)_2\overline{TiN=C(CMe_3)CH_2CH_2}$ 5 | a | 119.1 | (s) | |
| a b e f g d c | b | 12.0 | 126 (q) | |
| ($C_7D_8$, -20°) | c | 43.8 | 123 (t) | 33 (cd) |
| | d | 54.0 | 120 (t) | |
| | e | 175.2 | (s) | |
| | f | 39.7 | (s) | |
| | q | 29.1 | 125 (q) | |
| $(C_5Me_5)_2\overline{TiN=C(C_6H_4CH_3)CH_2CH_2}$ 6 | a | 120.2 | (s) | |
| a b e d c | b | 12.0 | 126 (q) | |
| | c | 42.7 | 122 (t) | |
|  | d | 55.7 | 122 (t) | 33 (cd) |
| f g h i j | e | 161.8 | (s) | |
| | f | 120.9 | (s) | |
| ($C_6D_{12}$; $C_7D_8$ for $^{13}C\{^1H\}$) | g | 126.4 | 158 (d) | |
| | h | 128.9 | 160 (d) | |
| | i | 137.0 | (s) | |
| | j | 21.3 | (obscured) | |

Table II (continued)

| | | | | | |
|---|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiNHC(CH_2CH_3)=CHCH_2}$ | 7 | a | 116.9 | | |
| a b e f g d c | | b | 11.6 | | |
| ($C_7D_8$) | | c | 61.2 | | 38 (cd) |
| | | d | 112.5 | | |
| | | e | 142.2 | | |
| | | f | 34.1 | | |
| | | g | 10.4 | | |
| $(C_5Me_5)_2\overline{TiCH=C(CH_3)CH_2CH_2}$ | 8 | a | 121.5 | (s) | |
| a b f e g d c | | b | 12.1 | 126 (q) | |
| ($C_7D_8$, -30°) | | c | 39.6 | 122 (t) | 31 (cd) |
| | | d | 55.6 | 123 (t) | |
| | | e | 136.3 | (s) | |
| | | f | 193.6 | 135 (d) | |
| | | g | 26.7 | 125 (q) | |
| $(C_5Me_5)_2Ti(C\equiv CCH_3)(CH_2CH_3)$ | 9 | a | 120.2 | (s) | |
| a b e fg c d | | b | 12.8 | 126 (q) | |
| ($C_7D_8$, -30°) | | c | 61.4 | 121 (t) | 33 (cd) |

Table II (continued)

| | | | | | |
|---|---|---|---|---|---|
| | | d | 22.6 | 123 (q) | |
| | | e | 148.8 | (s) | 4 (q) |
| | | f | 110.7 | (s) | 10 (q) |
| | | g | 6.4 | 129 (q) | |
| $(C_5Me_5)_2Ti(C{\equiv}CCMe_3)(CH_2CH_3)$ | 10 | a | 121.0 | | |
| a b e f g h c d | | b | 12.8 | | |
| | | c | 61.9 | | 32(cd) |
| ($C_7D_8$, -40°) | | d | 23.9 | | |
| | | e, f | not observed | | |
| | | g | 28.3 | | |
| | | h | 32.1 | | |
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(CH_3)CH_2CH_2}$ | 12 | a | 121.3 | (s) | |
| a b f g e h d c | | b | 12.2 | 126 (q) | |
| | | c | 38.5 | 121 (t) | 29 (cd) |
| ($C_6D_6$) | | d | 57.4 | 124 (t) | |
| | | e | 129.9 | (s) | |

Table II. (continued)

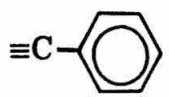
| | | | | | |
|---|---|---|---|---|---|
| | | f | 194.3 | (s) | |
| | | g | 18.8 | 124 (q) | |
| | | h | 21.6 | 123 (q) | |
| $(C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CCH_3)$ | 13 | a | 120.4 | (s) | |
| a b d c | | b | 11.9 | 126 (q) | |
| $(C_7D_8,\ -40°)$ | | c | 200.1 | (s) | 6 (q) |
| $(C_5Me_5)_2Ti(\eta\text{-}C_6H_5C{\equiv}CC_6H_5)$ | 14 | a | 122.4 | (s) | |
| a b | | b | 12.4 | 126 (q) | |
| | | c | 200.9 | (s) | 4 (t) |
|  | | d | 141.4 | (s) | 7 (t) |
| c de fg | | e | 128.7 | 157 (d) | 7 (t) |
| $(C_6D_{12})$ | | f | 128.1 | 157 (d) | 7 (d) |
| | | g | 125.1 | 160 (d) | 8 (t) |
| $(C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CCH_2CH_3)$ | 15 | a | 120.4 | | |
| a b c d ef g | | b | 11.8 | | |
| $(C_7D_8,\ -10°)$ | | c-g | not observed | | |

Table II. (continued)

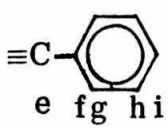
| | | | |
|---|---|---|---|
| $(C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CCH_2(CH_2)_3CH_3)$ | 16 | a | 121.0 |
| a b e c d f g h i j | | b | 11.8 |
| | | c | 195.8 |
| | | d | 199.7 |
| $(C_7D_8)$ | | e | 14.5 |
| | | f | 18.4 |
| | | g | 30.7 |
| | | h | 34.8 |
| | | i | 56.8 |
| $(C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CC_6H_5)$ | 17 | a | 121.3 |
| a b c d, e | | b | 12.1 |
| | | c | 19.7 |
|  | | d | 192.7 |
| | | e | 207.7 |
| $(C_6D_6)$ | | f | 141.1 |
| | | g-i | obscured |

Table II. (continued)

| | | | | |
|---|---|---|---|---|
| $(C_5Me_5)_2\overbrace{TiC(CH_3)=C(CH_2CH_3)CH_2CH_2}$ | 18$\alpha$ | a | 121.1 | |
| a b f g e h i d c | | b | 12.2 | |
| | | c | 35.4 | 30(cd) |
| | | d | 57.0 | |
| ($C_7D_8$) | | e | 136.5 | |
| | | f | 193.9 | |
| | | g | 26.0 | |
| | | h | 20.8 | |
| | | i | 13.5 | |
| $(C_5Me_5)_2\overbrace{TiC(CH_2CH_3)=C(CH_3)CH_2CH_2}$ | 18$\beta$ | a | 121.2 | |
| a b f g h e d c | | b | 12.4 | |
| | | c | 38.7 | 30(cd) |
| | | d | 60.0 | |
| ($C_7D_8$, -10°) | | e-h | not observed | |

Table II. (continued)

| | | | |
|---|---|---|---|
| $(C_5Me_5)_2\overbrace{TiC(CH_3)=C(CH_2(CH_2)_3CH_3)CH_2CH_2}$ 19α | a | 120.2 | |
| a b f g e h-k l d c | b | 12.3 | |
| | c | 36.2 | 30 (cd) |
| | d | 57.4 | |
| $(C_7D_8)$ | e | 135.5 | |
| | f | 194.6 | |
| | g | 20.9 | |
| | h | 23.2 | |
| | i | 29.0 | |
| | j | 33.2 | |
| | k | 33.5 | |
| | l | 14.3 | |
| $(C_5Me_5)_2\overbrace{TiC(n\text{-}C_5H_{11})=C(CH_3)CH_2CH_2}$ 19β | a | 121.4 | |
| a b e h-l f g d c | b | 12.5 | |
| | c | 38.7 | 31 (cd) |
| | d | 60.4 | |
| | e-l | not observed | |

Table II. (continued)

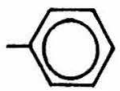
| | | | | | |
|---|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(C_6H_5)CH_2CH_2}$ 20α | a | 121.6 | | | |
| a b e f g h-k d c | b | 12.3 | | | |
| | c | 38.9 | | 29 (cd) | |
| | d | 57.2 | | | |
|  | e | 198.0 | | | |
| e h i jk | f | 22.4 | | | |
| $(C_6D_6)$ | g | 146.4 | | | |
| | h | 137.3 | | | |
| | i | obscured | | | |
| | j | 125.1 | | | |
| | k | obscured | | | |
| $(C_5Me_5)_2\overline{TiOC(O)CH_2CH_2}$ 22 | a | 124.1 | (s) | | |
| a b e d c | b | 11.6 | 126 (q) | | |
| | c | 54.0 | 128 (t) | | |
| $(C_6D_6)$ | d | 53.6 | 125 (t) | 52 (de) | |
| | e | 171.5 | (s) | | 6 (quin) |

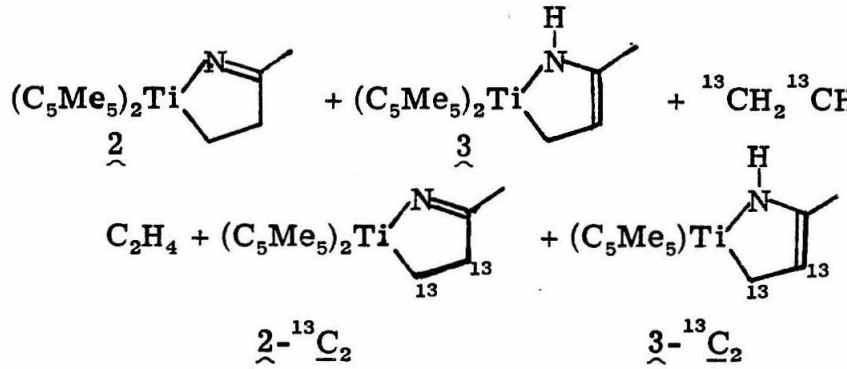
Table II. (continued)

| | | | | |
|---|---|---|---|---|
| $(C_5Me_5)(C_5Me_5)\overline{TiOC(CH_3)CH_2CH_2}$ 23 | a | 121.3 | (s) | |
| a c b d g h f e | b | 121.0 | (s) | |
| $(C_6D_6)$ | c | 12.1 | 126 (q) | |
| | d | 12.2 | 126 (q) | |
| | e | 55.8 | 121 (t) | 31 (ef) |
| | f | 52.7 | 127 (t) | |
| | g | 75.8 | 138 (d) | |
| | h | 25.9 | 124 (q) | 4(d) |

*Sample temperature 34° unless given.

‡Long range $J_{C-C}$ values.

coupling constants (Table II), is found to be reversible. Incorporation of $^{13}CH_2{}^{13}CH_2$ into 2 is not detected ($^1H$ and $^{13}C$ NMR) when the addition of $CH_3CN$ to 1 (eq. 1) is carried out at -50° in the presence of one equivalent of $^{13}CH_2{}^{13}CH_2$. At 25°, however, unlabelled ethylene and $^{13}C$ enriched 2 and 3 are slowly formed (eq. 4), demonstrating that

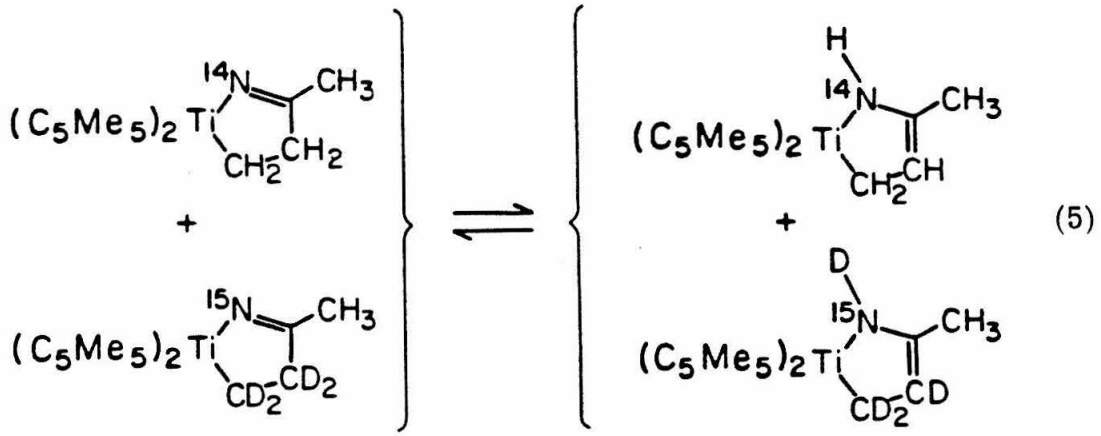



(4)

ethylene exchange can occur subsequent to the formation of 2 and 3. This ligand lability may be responsible for the rapid decomposition which occurs when solutions of 2 and 3 are warmed above 40° or are exposed above -20° to CO, excess nitrile, or vacuum. In all cases, varying amounts of $C_2H_4$ are detected ($^1H$ and $^{13}C$ NMR) along with several diamagnetic and paramagnetic products which have not been identified.

As a dry solid, 2 can be stored for months at -20° and handled for short periods at 25° without decomposition or formation of 3. Although the limited stability of 2 has frustrated attempts to obtain an elemental analysis, 2 is sufficiently stable to permit the low temperature preparation of a toluene-$d_8$ solution containing both doubly labelled $(\eta\text{-}C_5Me_5)_2\overline{Ti^{15}N{=}C(CH_3)CD_2CD_2}$ (2-$^{15}$N, $d_4$) and unlabelled 2 ([2-$^{15}$N, $d_4$]/[2] = 1.2 ± 0.4). Warming the sample to 0°, the

imine ⇌ enamine tautomerization was measured by the intensities of the $C_5Me_5$ resonances of $\underset{\wedge}{3}$ and $\underset{\wedge}{2}$ while the hydrogen-deuterium scrambling was monitored by the intensities of the $^{14}N$-H and $^{15}N$-H resonances of $\underset{\wedge}{3}$-$^{14}\underline{N}$ and $\underset{\wedge}{3}$-$^{15}\underline{N}$ ($^1J_{^{15}N\text{-}H}$ = 72 Hz). Although some decomposition (< 3%) is detected in the latter stage of the experiment, the extent of H-D scrambling observed in the products (column 5, Table III) is small in comparison to the extent of equilibrium reached between imine and enamine complexes (column 3). Thus, the imine ⇌ enamine tautomerization appears to proceed by a mechanism which does not involve hydrogen exchange (eq. 5).




(5)

Table III. Imine ⇌ Enamine Crossover Experiment

| Time (min) | $\frac{[\underset{\frown}{3}]}{[\underset{\frown}{2}]}$ | Extent of Equilibration[a] | $\frac{[\underset{\frown}{3}\text{-}^{15}\underline{\underline{NH}}]}{[\underset{\frown}{3}\text{-}^{14}\underline{\underline{NH}}]}$ | Extent of Scrambling[b] |
|---|---|---|---|---|
| 0 | $< 0.02$ | $< 0.05$ | $\ll 0.05$ | -- |
| 7 | 0.03 (1) | 0.08 | $\ll 0.05$ | -- |
| 15 | 0.07 (4) | 0.19 | $< 0.05$ | $< 0.04$ |
| 34 | 0.22 (3) | 0.56 | 0.07 (4) | 0.06 |
| 48 | -- | -- | 0.10 (4) | 0.08 |
| 71 | 0.25 (2) | 0.64 | -- | -- |
| 83 | 0.27 (2) | 0.68 | 0.12 (4) | 0.10 |
| 106 | 0.28 (2) | 0.72 | 0.14 (4) | 0.12 |
| 440 | 0.35 (2) | 0.90 | 0.27 (3) | 0.23 |

[a] $\frac{[\underset{\frown}{3}]/[\underset{\frown}{2}]}{K_{eq}}$, where $K_{eq} = 0.39 \pm 0.02$ at 0°.

[b] $\frac{[\underset{\frown}{3}\text{-}^{15}\underline{\underline{NH}}]/[\underset{\frown}{3}\text{-}^{14}\underline{\underline{NH}}]}{S_{eq}}$, where $S_{eq} = 1.2 \pm 0.4$ (statistical scrambling ratio from initial $[\underset{\frown}{2}\text{-}^{15}\underline{N}, d_4]/[\underset{\frown}{2}]$).

Propionitrile, trimethylacetonitrile, and p-tolunitrile react with 1 to yield the corresponding metallacycloimines, $(\eta\text{-}C_5Me_5)_2\overline{TiN=C(R)CH_2CH_2}$, where R = $CH_2CH_3$ (4), $C(CH_3)_3$ (5), and

$$(C_5Me_5)_2Ti(C_2H_4) + RCN \rightarrow (C_5Me_5)_2Ti\langle N=C(R)CH_2CH_2 \rangle \quad (6)$$

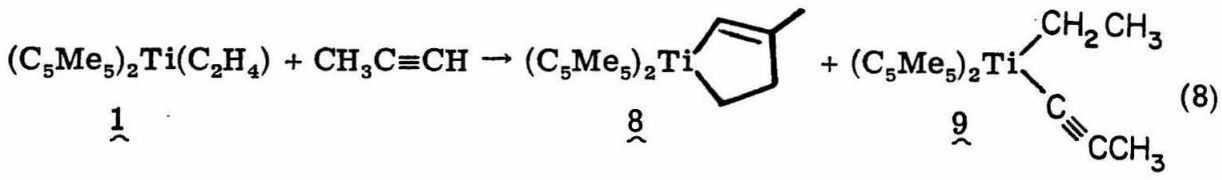
p-$CH_3C_6H_4$ (6), respectively. While 4, 5, and 6 have IR and NMR spectra which closely resemble those of 2, these derivatives are more stable in the solid state than 2 and have been fully characterized. The ethyl metallacycloimine 4 tautomerizes to a small extent ($K_{eq}$ = 0.10 at 25°), yielding $(\eta\text{-}C_5Me_5)_2\overline{TiNHC(CH_2CH_3)=CHCH_2}$ (7) which has been

$$(C_5Me_5)_2Ti\langle N=C(CH_2CH_3)CH_2CH_2 \rangle \rightleftharpoons (C_5Me_5)_2Ti\langle NH-C(CH_2CH_3)=CHCH_2 \rangle \quad (7)$$

4 7

characterized in solution by $^1H$ and $^{13}C$ NMR. No isomerization of 5 or 6 is observed even after several weeks at 25° (detection limit $K_{eq} \leq 0.01$). As observed for 2, solutions of 4, 5, and 6 release ethylene and decompose to a multitude of titanium containing species, although for 5 and 6, this requires several months at ambient temperature.

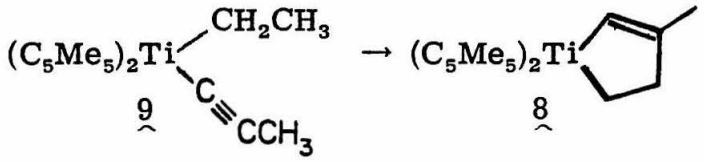
Reactions of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with Alkynes. The titanium ethylene complex rapidly reacts at -50° with one equivalent of propyne, affording approximately equal amounts of the metallacyclopentene complex, $(\eta\text{-}C_5Me_5)_2\overline{TiCH=C(CH_3)CH_2CH_2}$ (8), and an acetylide ethyl species, $(\eta\text{-}C_5Me_5)_2Ti(C\equiv CCH_3)(CH_2CH_3)$ (9). Spectroscopic data




1 8 9 (8)

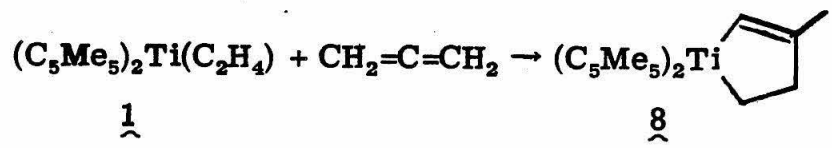
($\nu_{C=C}$ = 1587, $\nu_{C\equiv C}$ = 2100; NMR, Tables I and II) are consistent with the structures shown (eq. 8). The $\alpha$-methyl isomer of 8, $(\eta\text{-}C_5Me_5)_2\overline{TiC(CH_3)=CHCH_2CH_2}$, is not observed, presumably due to unfavorable steric interactions between the methyl group and the $C_5Me_5$ ligands. Formation of 8 and 9 proceeds without loss of ethylene from the titanium center since the addition of propyne to a solution of 1 containing 0.6 equivalents $^{13}CH_2{}^{13}CH_2$ does not lead to incorporation of labelled ethylene into the products, either initially at -50° or after several hours at 25°.

In solution, the acetylide ethyl compound undergoes a very slow rearrangement to 8 at 25° (eq. 9). Isomerization of 9, subsequent to




9 8 (9)

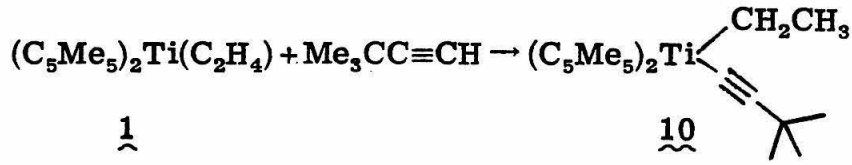
the initial formation of 8 and 9, provides a quantitative, albeit slow conversion of 1 and $CH_3C\equiv CH$ to 8 and facilitates its isolation as a slightly air sensitive, crystalline solid. The metallacyclopentene complex 8 is also slowly formed (ca. 80% pure by NMR) upon addition of allene to toluene solutions of 1 at 25° (eq. 10). The course of this reaction is not known; however, the isomerization of allene to propyne



(10)

may proceed by a mechanism similar to that of the isomerization of olefins with 1,[1] where the final step involves the $\beta$-hydrogen abstraction of a vinylic hydrogen.[2]

Two other acetylide alkyl compounds have been prepared. Treatment of a toluene solution of 1 with one equivalent of $Me_3CC{\equiv}CH$ at -40° quantitatively affords $(\eta\text{-}C_5Me_5)_2Ti(C{\equiv}CCMe_3)(CH_2CH_3)$ (10). Rearrangement of 10 to a metallacyclopentene structure is not observed



(11)

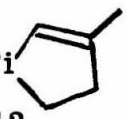
even after weeks at 25°. Both 10 and a methyl analogue, $(\eta\text{-}C_5Me_5)_2Ti(C{\equiv}CCMe_3)(CH_3)$ (11), which forms as the major product (ca. 80%) from the reaction of $(\eta\text{-}C_5Me_5)_2TiI(CH_3)$ with $LiC{\equiv}CCMe_3$, are isolated as oily red solids and characterized by IR and NMR spectroscopy.

In contrast to the rapid reactions which occur below -30° between the titanium ethylene complex and terminal acetylenes, disubstituted acetylenes slowly form the corresponding 2,3-disubstituted metallacyclopentenes at ≥ 25°. The reaction of 1 with excess 2-butyne quantitatively yields $(\eta\text{-}C_5Me_5)_2TiC(CH_3){=}C(CH_3)CH_2CH_2$ (12) after ca. 8 h at 25°. Red-orange 12 is isolable as a stable, crystalline solid

which very slowly decomposes in benzene solution at 80° (< 10% decomposition after one week). During the preparation of 12 (eq. 12),

$$(C_5Me_5)_2Ti(C_2H_4) + CH_3C{\equiv}CCH_3 \rightarrow (C_5Me_5)_2Ti\langle \quad \rangle \qquad (12)$$

1 12



traces of $C_2H_4$ and an acetylene adduct, $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CCH_3)$ (13), are detected by NMR. Thermally unstable 13 can be prepared independently by addition of 2-butyne to $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ and has been characterized spectroscopically.[3] Treatment of 1 with diphenylacetylene yields the alkyne adduct, $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}PhC{\equiv}CPh)$ (14),[3] and $C_2H_4$ (eq. 13). No diphenylmetallacyclopentene is formed even at

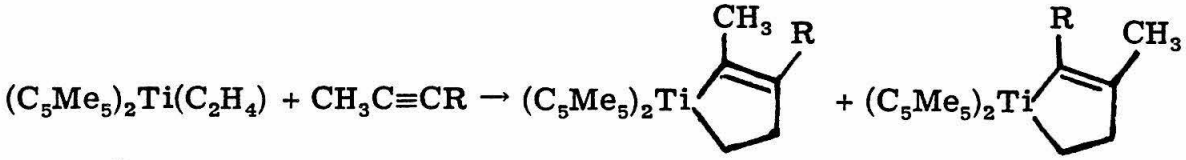
$$(C_5Me_5)_2Ti(C_2H_4) + PhC{\equiv}CPh \rightarrow (C_5Me_5)_2Ti(PhC{\equiv}CPh) + C_2H_4 \qquad (13)$$

1 14

elevated temperatures under excess ethylene. Like 13, monomeric 14 exhibits a low C≡C stretch in the IR: $\nu_{C\equiv C}$ = 1683 $cm^{-1}$, 13; $\nu_{C\equiv C}$ = 1647 $cm^{-1}$, 14.

The reactions of other alkynes with 1 involve both ligand substitution, as seen with PhC≡CPh, and alkyne addition to form titanacyclopentenes, as seen with MeC≡CMe. Addition of 2-pentyne, 2-octyne, and 1-phenylpropyne to solutions of 1 give appreciable concentrations of the transient alkyne adducts, $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}CH_3C{\equiv}CR)$ (where R = ethyl (15), n-pentyl (16), phenyl (17), respectively), prior to formation of the corresponding metallacyclopentenes (18, 19, and 20). The alkyne compounds 15, 16, and 17 have been characterized by $^{13}C$ NMR but have not

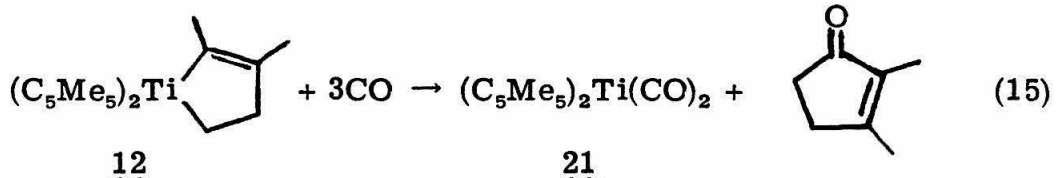
been prepared independently and isolated. Since the two substituents on these acetylenes are dissimilar, the metallacyclopentenes produced may be a mixture of two isomers (eq. 14). The isomer ratio of 18



(14)

formed at 25° is 80 : 20 ($^{13}$C NMR); for 19, the ratio formed at 25° is 85 : 15, while the preparation of 20 at 80° yields a ca. 95 : 5 mixture. Based on $^{1}$H NMR data, the major isomer in each case is believed to be the $\alpha$ isomer, although this has not been confirmed. Partial decomposition of the sample and depletion of the minor isomer occur when a solution of 18$\alpha$ and 18$\beta$ is warmed for two weeks at 50°.

Carbonylation (3 atm) of $(\eta\text{-}C_5Me_5)_2\overline{TiCH=C(CH_3)CH_2CH_2}$ (8) occurs within 18 h at 80° to afford $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$ (21)[4] in high yield. Although the fate of the organic fragment from this reaction has not been firmly established, the analogous carbonylation of $(\eta\text{-}C_5Me_5)_2\overline{TiC(CH_3)=C(CH_3)CH_2CH_2}$ (12) yields 21 and 2,3-dimethyl-2-cyclopentenone[5] quantitatively by NMR (eq. 15). Attempts to form the



(15)

cyclopentenone and/or 12 starting from the dicarbonyl complex 21 have not proven successful.

Reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with Carbonyl Compounds.

The titanium ethylene complex reacts rapidly at -78° with one equivalent of carbon dioxide affording a bright red metallalactone, $(\eta\text{-}C_5Me_5)_2\overline{TiOC(O)CH_2CH_2}$ (22), in high yield (eq. 16). Monomeric 16

$$(C_5Me_5)_2Ti(C_2H_4) + CO_2 \rightarrow (C_5Me_5)_2Ti\text{-}\overline{OC(O)CH_2CH_2} \qquad (16)$$

1 22

contains an uncoordinated carbonyl, as evidenced by $\nu_{C=O} = 1652\ cm^{-1}$ in the infrared spectrum. The $^1H$ and $^{13}C$ NMR spectra are readily assigned; the $^{13}C$-$^{13}C$ coupling constant of 52 Hz between $\beta$-methylene carbon and the lactone carbon clearly establishes the formation of the C-C bond in 22. Solid or solution samples of 22 are thermally robust but decompose very slowly upon exposure to visible light. Above 0°, the carboxylation of 1 ($CO_2$ : 1 = 1) does not produce 22. Under these conditions, a brown solution forms from which a light-colored solid precipitates. Free ethylene and 1 are found in solution together with a number of other, unidentified products.

Acetaldehyde reacts rapidly below -20° to yield the alkoxy complex, $(\eta\text{-}C_5Me_5)_2\overline{TiOCH(CH_3)CH_2CH_2}$ (23). The 90 MHz $^1H$ NMR spectrum for 23 is characteristic for the structure shown (eq. 17),

$$(C_5Me_5)_2Ti(C_2H_4) + CH_3CHO \rightarrow (C_5Me_5)'(C_5Me_5)Ti\text{-}\overline{OCH(CH_3)CH_2CH_2} \qquad (17)$$

having one resonance for each of the inequivalent $C_5Me_5$ rings and a doublet for the alkoxy methyl. At 500 MHz, the six highly coupled

hydrogen resonances of the $\overline{\text{TiOCH(CH}_3\text{)CHH'CHH'}}$ moiety are observed (Table I). IR and $^{13}C$ NMR spectra also are consistent with this formulation. Formation of the acyl ethyl isomer, $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(COCH}_3\text{)(CH}_2\text{CH}_3\text{)}$, is not observed even at -60°. The bright orange-red 23 is stable in the solid state or solution indefinitely at 25°.

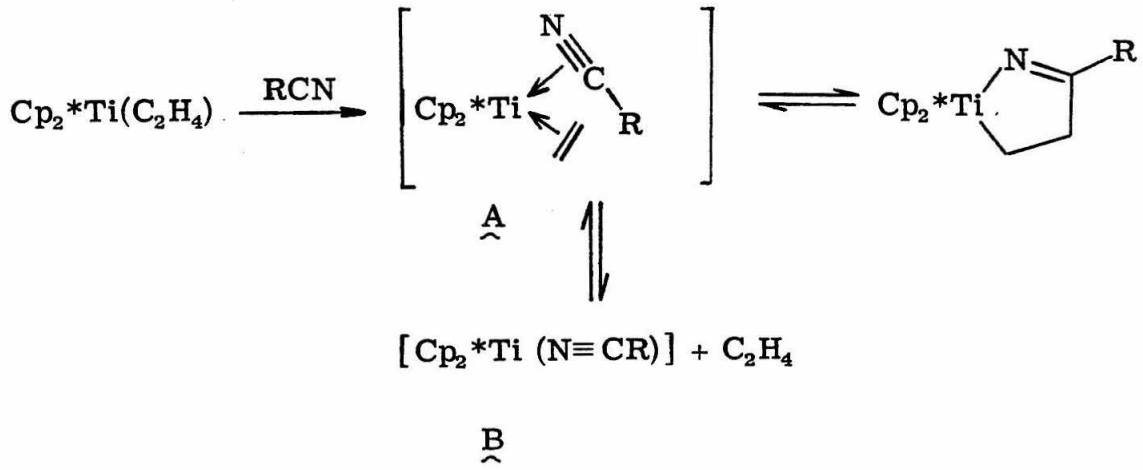
Acetone does not react with 1 below 0°. After warming a toluene solution of acetone and 1 (1.1 mol $C_3H_6O$/mol 1) to 25°, free ethylene is detected along with ca. 0.4 equivalents 1 and several other titanium species. Although not fully characterized, the most abundant product appears to contain an isopropoxy group. No resonances which may be attributed to $(\eta\text{-C}_5\text{Me}_5)_2\overline{\text{TiOC(CH}_3\text{)}_2\text{CH}_2\text{CH}_2}$ are discernible from the $^1H$ NMR spectrum.

The mechanistic implications these results have with regard to the reactivity of $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$ are treated in the following section.

Discussion

Bis(pentamethylcyclopentadienyl)titanium ethylene (1) has been found to react with a variety of unsaturated organic compounds by three basic reaction types. The most common reaction, oxidative coupling of an added substrate with the titanium and the ethylene ligand to form a five-membered Ti(IV) metallacyclic product, readily occurs with sterically unhindered substrate compounds. In the case of alkyl and aryl nitriles, 1 rapidly adds one equivalent of substrate at low temperature, giving a Ti(IV) metallacycloimine complex. As demonstrated by the exchange experiments with labelled ethylene, the reaction between 1 and acetonitrile occurs without loss of ethylene from the metal center. Thus an associative reaction pathway, possibly involving A as an intermediate, is suggested (Scheme 1). The slow exchange of free ethylene

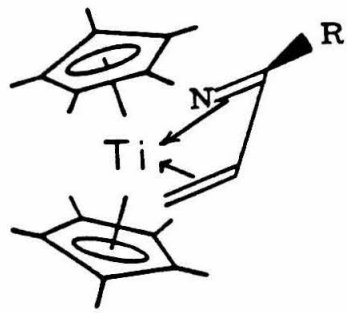
Scheme 1



with the imine complex (2), and the observed loss of $C_2H_4$ from 2 when the imine is placed under vacuum are consistent with dissociative ethylene exchange via a nitrile intermediate B as shown ($Cp^* = C_5Me_5$). A mononitrile species analogous to B, $(\eta\text{-}C_5Me_5)_2Zr(N{\equiv}CC_6H_4CH_3)$, has been spectroscopically observed.[6]

Partial isomerization of $(\eta\text{-}C_5Me_5)_2\overline{TiN{=}C(R)CH_2CH_2}$ to the tautomeric enamines, $(\eta\text{-}C_5Me_5)_2\overline{TiNHC(R){=}CHCH_2}$, occurs when the R is a methyl or ethyl substituent but not when R is a t-butyl or p-tolyl group. Such behavior is not consistent with the reactivity being influenced by electronic effects, since the influence of the t-butyl group would be expected to be similar to that of the methyl and ethyl substituents. The imine $\rightleftharpoons$ enamine tautomerization is formally a 1, 3 hydrogen shift and thus a symmetry forbidden reaction. The transformation is readily catalyzed by even traces of acid or base, however.[7] Noting that the Ti(IV) center is a potential catalyst for the isomerization, a crossover experiment was performed to test whether the tautomerization proceeds intramolecularly or is externally catalyzed. The results in Table III clearly show that some H-D scrambling occurs during the tautomerization. However, the 2 $\rightleftharpoons$ 3 reaction proceeds ca. six times faster than the rate of hydrogen scrambling. Since it would be necessary to postulate a remarkably large inverse isotope effect ($k_D/k_H \geq 6$) in order to consider these results appropriate for an externally catalyzed reaction (involving either a second titanium-containing species or a fortuitous acid or base), it appears that the tautomerization follows an intramolecular pathway.

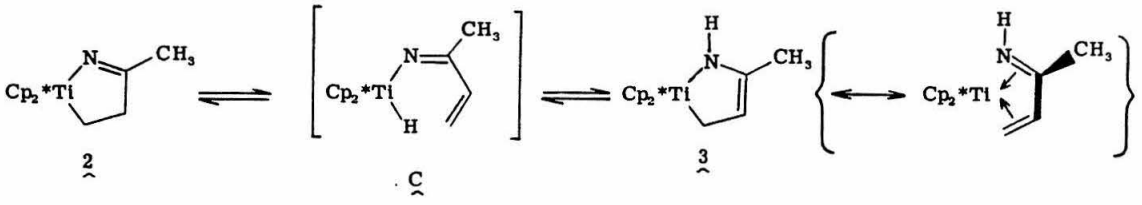
Formation of the enamines decreases along the series, $CH_3 > C_2H_5 \gg \underline{t}\text{-}C_4H_9 \simeq \underline{p}\text{-}CH_3C_6H_4$, suggesting that either the substituents exert a steric influence on the rearrangement or the reaction proceeds via an exo-methylene intermediate, a species not attainable for metallacycloimines having t-butyl or p-tolyl substituents. Isomerization of $(\eta\text{-}C_5Me_5)_2\overline{TiN=C(CD_3)CH_2CH_2}$ ($\underset{\sim}{2}\text{-}\underline{d}_3$) affords only $(\eta\text{-}C_5Me_5)_2\overline{TiNHC(CD_3)=CHCH_2}$ ($\underset{\sim}{3}\text{-}\underline{d}_3$) with no detectable H-D scrambling. This result eliminates the possibility that the tautomerization of the titanacycloimine proceeds via an exo-methylene intermediate, since such a pathway would result in scrambling of the deuteriums and hydrogens in the labelled imine and enamine complexes. Alternatively, steric control of the equilibria appears to be reasonable and may reflect the non-planarity of the metallacycloenamine ring in these structures. Consideration of the metallacycloenamine as having partial titanium azabutadiene character would account for deviations from a planar structure and may be rationalized as a way in which the formally sixteen-electron titanium might achieve a closed shell configuration. The decidedly non-planar $\overline{TiSC=CS}$ rings in the structures



of $(\eta\text{-}C_5H_3)_2\overline{TiSCH=CHS}$ and $(\eta\text{-}C_5H_5)_2\overline{TiS\text{-}C_6H_4\text{-}S}$ have been attributed to similar pairs of resonance structures.[8] The incomplete isomerization of the imines to the enamine complexes and their general instability seem to preclude structural investigations of these particular compounds, however.

These results are in accord with an intramolecular rearrangement in which the titanium promotes the hydrogen shift. A simple mechanism is outline in Scheme 2.

Scheme 2

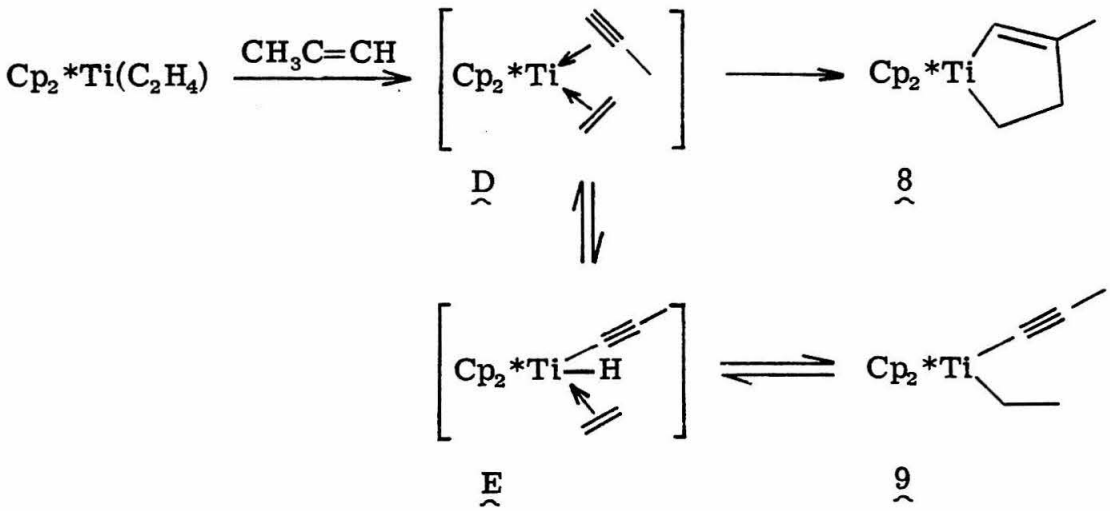



2 C 3

The addition of alkynes to the titanium ethylene complex produces metallacyclopentene compounds analogous to the metallacycloimine species. Two other reactions appear to be competitive with oxidative coupling, however. Internal acetylenes displace ethylene ligand in 1 to form $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-acetylene})$ species while formal oxidative addition of terminal acetylenic C-H bonds by 1 give titanium acetylide ethyl complexes. The addition of propyne to solutions of 1 yields approxi-

mately equal amounts of the coupling product, $(\eta\text{-}C_5Me_5)_2\overline{TiCH=C(CH_3)CH_2CH_2}$ (8), and the oxidative addition product, $(\eta\text{-}C_5Me_5)_2Ti(C\equiv CCH_3)(C_2H_5)$ (9). While the initial ratio of 8 : 9 varies slightly with changes in temperature and solvent, formation of both 8 and 9 occurs without loss of ethylene, as demonstrated by the labelling studies with $^{13}C_2H_4$. Moreover, the subsequent rearrangement of 9 to 8 occurs very slowly even at 25° whereas the initial products are formed upon mixing below -50°. Based on these data, the products, 8 and 9, are believed to be derived from parallel pathways which have similar energies of activation. One possible mechanism is outlined in Scheme 3.[9]

Scheme 3



Disubstituted metallacyclopentenes are slowly produced by addition of internal alkynes to 1. Unlike the oxidative coupling of 1 with propyne, these reactions often are not competitive with ethylene displacement, since free ethylene and the corresponding acetylene adducts are detected as transient species. In the case of diphenylacetylene, no metallacyclopentene complex is formed and $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_6H_5C{\equiv}CC_6H_5)$ (14) and ethylene are produced quantitatively. With the exception of 14, readdition of ethylene to the titanium acetylene compounds is observed, with formation of the metallacyclopentenes proceeding to completion.

Interestingly, the coupling of two alkynes by the decamethyltitanocene species is not observed in the presence of excess alkyne even at elevated temperatures. Such behavior differs significantly from that found for the parent titanocene moiety, $(\eta\text{-}C_5H_5)_2Ti$, which readily couples two alkynes to form the very robust metallacyclopentadiene derivatives.[10] This difference has been noted previously for bis-(pentamethylcyclopentadienyl)titanium and zirconium complexes and has been attributed to increased steric crowding around the metal centers.[3,11]

The stability of the carbon-carbon bond between the ethylene and alkyne substrates is utilized in the carbonylation reaction of $(\eta\text{-}C_5Me_5)_2\overline{TiC(CH_3)=C(CH_3)CH_2CH_2}$ (12). Unlike the reaction of CO with $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$, which results in ethylene dissociation, the reaction of 12 with CO is analogous to the insertion, reductive elimination behavior observed for other dialkyl and diaryl derivatives of Ti(IV).[12] In this instance, however, the titanium compound 12 is a

vinyl alkyl complex derived from a Ti(II) $\pi$-olefin species. Thus, 2,3-dimethyl-2-cyclopentenone is produced stoichiometrically from ethylene, 1-butyne, and carbon monoxide.

The trends observed for the reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with nitriles and acetylenes substrates are also found to be valid for the reactions of $\underset{\frown}{1}$ with carbonyl compounds. The oxidative coupling of carbon dioxide with $\underset{\frown}{1}$ produces the Ti-O bonded complex, $(\eta\text{-}C_5Me_5)_2\overline{TiOC(O)CH_2CH_2}$, at -78°. Acetaldehyde similarly affords a metallacyclic product at somewhat high temperature while the sterically larger acetone only reacts with $\underset{\frown}{1}$ at temperatures where ethylene loss and formation of the titanium fulvene hydride compound, $(\eta\text{-}C_5Me_5)(\eta\text{-}C_5Me_4CH_2)TiH$,[13] are appreciable.

The reactions of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with a variety of sterically unhindered unsaturated organic substrates are found to proceed without loss of ethylene from the titanium. By far the most common reaction is the oxidative coupling of the substrates with $\underset{\frown}{1}$ to produce five-membered metallacyclic complexes. Organic molecules having double bonds rather than triple bonds afford stable products, at least in the case of oxygenates which are capable of forming a strong Ti-O bond. Displacement of the ethylene ligand, as observed with diphenylacetylene, and formal oxidative addition of an active C-H bond may also occur. Finally, the metallacyclic compounds are able to undergo subsequent chemistry involving carbonylation and reductive elimination, as demonstrated by the formation of cyclopentenone and $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$ or intramolecular isomerization, as exhibited by the metallacycloimine species.

## Experimental Section

General Considerations. All manipulations were performed using glove box or high vacuum line techniques. Argon, nitrogen, and hydrogen were purified by passage over MnO on vermiculite and activated Linde 4Å molecular sieves. Solvents were purified by vacuum transfer, first from $LiAlH_4$, then "titanocene."[14] Benzene-$\underline{d}_6$, cyclohexane-$\underline{d}_{12}$, and toluene-$\underline{d}_8$ (Aldrich, Stohler) were dried over molecular sieves and vacuum transferred from "titanocene." Propyne, 2-butyne, 2-pentyne, and 3,3-dimethyl-1-butyne (all Farchan), ethylene, allene, and acetaldehyde were freeze-pump-thaw degassed at -196°. Methyl iodide, $CD_3CN$ (99% D, Kor), $^{13}CH_3CN$ (90% $^{13}C$, Stohler), and all other nitriles were vacuum transferred from $CaH_2$. Acetonitrile-1-$^{13}C$ and $CH_3C^{15}N$ were prepared by addition of methyl iodide to a toluene solution containing 18-crown-6 and $Na^{13}CN$ (91.5% $^{13}C$, Prochem) or $KC^{15}N$ (99% $^{15}N$, Koch), respectively.[15] Carbon dioxide and carbon monoxide were used directly from the cylinder. Ethylene-$^{13}\underline{C}_2$ (90% $^{13}C$, Merck, Sharp, and Dohme) and ethylene-$\underline{d}_4$ (98% D, Stohler) were freeze-pump-freeze-thaw degassed at -196° and distilled at -78°. 1-Phenyl-propyne and acetone were distilled from molecular sieves; diphenylacetylene was recrystallized from diethyl ether. $[(\eta\text{-}C_5Me_5)_2Ti]_2(\eta\text{-}N_2)$,[13] $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$,[1] and $(\eta\text{-}C_5Me_5)_2TiI(CH_3)$[1] were prepared by previously reported methods.

Proton, $^2H$, and $^{13}C$ NMR spectra were recorded using Varian EM-390, JEOL FX90Q, and Bruker WM-500[16] spectrometers. Spectra were taken in benzene or toluene solutions, and data are referenced to

$Me_4Si$ at 0 δ. Infrared spectra were obtained using a Beckman 4240 spectrophotometer. Spectra of solids were recorded as nujol mulls using KBr plates, spectra of gases were measured using a 10 cm path length cell (NaCl windows) fitted with a stopcock and ball joint for attachment to a vacuum line. Molecular weights were determined cryoscopically or by vapor phase osmometry. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories, Germany.

Procedure: A majority of the experiments were performed by procedures similar to those detailed for 2. Isolated yields are generally reduced from those observed spectroscopically due to the high solubility of the compounds. Analytical data are collected in Table IV, $^1H$ and $^{13}C$ NMR data are found in Tables I and II, respectively.

$(\eta\text{-}C_5Me_5)_2\overline{TiN{=}C(CH_3)CH_2CH_2}$ (2). Toluene-$d_8$ (0.3 mL) and $CH_3CN$ (0.073 mmol) were condensed at -196° into an NMR tube containing 1 (0.069 mmol). The mixture was warmed to -78° and the reaction monitored by $^1H$ and $^{13}C$ NMR between -70 and 30°.

Petroleum ether (7 mL) and acetonitrile (0.88 mmol) were condensed at -196° into a 10 mL flask containing 1 (230 mg, 0.66 mmol). The mixture was warmed to -40° and stirred 30 min, then cooled to -78°. The slurry of red-orange crystals was filtered and dried below -30°, affording 160 mg 2 (62%). IR 9from sample containing 2 and 3): 3370 (w), 2725 (w), 1638 (s), 1571 (m), 1280 (m), 1148 (m), 1020 (s), 645 (s), 617 (s), 595 (s), 517 (s) $cm^{-1}$. Similar procedures were employed for the isolation of $(\eta\text{-}C_5Me_5)_2\overline{TiN{=}C(C_2H_5)CH_2CH_2}$ (4), $(\eta\text{-}C_5Me_5)_2\overline{TiN{=}C(CMe_3)CH_2CH_2}$ (5) and $(\eta\text{-}C_5Me_5)_2\overline{TiN{=}C(C_6H_4CH_3)CH_2CH_2}$

(6). Yield of 4, 86%: IR; 2722 (w), 1640 (s), 1278 (s), 1100 (s), 1020 (s), 942 (m), 663 (s), 510 (s) $cm^{-1}$. Yield of 5, 56%: IR; 1620 (s), 1283 (w), 1055 (m), 1020 (m), 950 (m), 635 (m) $cm^{-1}$. Yield of 6, 28%: IR; 2725 (w), 1680 (s), 1555 (w), 1215 (s), 1022 (s), 830 (s), 455 (m) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2\overline{TiCH=C(CH_3)CH_2CH_2}$ (8) and $(\eta\text{-}C_5Me_5)_2Ti(C{\equiv}CCH_3)(C_2H_5)$ (9). Toluene (10 mL) and propyne (2.0 mmol) were condensed into a flask containing 1 (700 mg, 2.02 mmol). The solution was warmed to 25° and stirred overnight. Volatiles were removed in vacuo and the red-orange residue was recrystallized from octane to yield an 80:20 mixture of 8 and 9. Samples left in solution contained no 9 ($^1H$ NMR) after several days while the concentration of 8 increased proportionally vs. an internal standard. Isolated yield of 8: 450 mg (58%). IR (8): 2725 (w), 1587 (m), 1495 (m), 1312 (w), 1023 (s), 400 (s) $cm^{-1}$. IR (9): 2720 (w), 2100 (s), 1115 (m), 1023 (s), 973 (s) $cm^{-1}$. Addition of $CMe_3C{\equiv}CH$ to 1 similarly gives $(\eta\text{-}C_5Me_5)_2Ti(C{\equiv}CCMe_3)(C_2H_5)$ (10) as determined by NMR.

$(\eta\text{-}C_5Me_5)_2Ti(C{\equiv}CCMe_3)(CH_3)$ (11). Diethyl ether (10 mL) was condensed at -196° into a flask containing $(\eta\text{-}C_5Me_5)_2TiI(CH_3)$ (200 mg, 0.43 mmol) and $LiC{\equiv}CCMe_3$ (40 mg, 0.45 mmol). The mixture was warmed to 25° and stirred 4 h. Volatiles were removed in vacuo and the red-orange residue was treated to petroleum ether and vacuum repeatedly to remove the remaining diethyl ether. Petroleum ether solution was filtered and dried in vacuo to afford 11 as an oily red solid in ca. 60% yield. IR: 2720 (w), 2070 (s), 1365 (s), 1242 (s), 1200 (m), 1021 (s), 725 (s), 450 (m), 427 (m) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2TiC(CH_3)=C(CH_3)CH_2CH_2$ (12). Toluene (5 mL), 2-butyne (8 mmol), and ethylene (2 mmol) were condensed at -196° into a flask containing 1 (250 mg, 0.72 mmol). The mixture was warmed to 25° and stirred 12 h. Volatiles were removed under vacuum at 0° to yield a crude red-orange solid which was recrystallized from petroleum ether. Yield (two crops): 200 mg (70%). IR: 2795 (w), 2720 (w), 1580 (m), 1492 (m), 1020 (s), 590 (w) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_6H_5C{\equiv}CC_6H_5)$ (14). Cyclohexane-$d_{12}$ (0.3 mL) was condensed at -78° into an NMR tube containing 1 (75 mg, 0.22 mmol) an diphenylacetylene (50 mg, 0.28 mmol). The tube was sealed and placed in an oil bath at 80° for 45 min at which time the formation of 14 was found to be complete. No reaction with excess PhC≡CPh or $C_2H_4$ was observed after four months at 80°. Isolated yield: 40%. IR: 3070 (m), 3055 (m), 3020 (m), 2720 (w), 1647 (s), 1578 (s), 1070 (m), 1024 (s), 755 (vs), 690 (vs), 418 (m) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2TiC(CH_3)=C(C_2H_5)CH_2CH_2$ (18). Excess 2-pentyne (2 mL) was condensed at -196° onto a frozen solution of 1 (210 mg, 0.61 mmol) in toluene (10 mL). The mixture was warmed to 60° and stirred 6 h. The resulting yellow-brown solution was cooled to -196° and ethylene (1.6 mmol) was added. The solution was warmed to 25° and stirred overnight. The volatiles were removed in vacuo to give a red-orange solid which was recrystallized from cold petroleum ether, affording 18 in 15% yield. IR: 2787 (s), 2720 (w), 1577 (m), 1495 (m), 1020 (s) $cm^{-1}$. A similar procedure was used to prepare $(\eta\text{-}C_5Me_5)_2TiC(CH_3)=C(C_6H_5)CH_2CH_2$ (20) except that the reaction was

carried out at 90° for 20 h. Yield of 20, 31%: IR: 3070 (w), 3050 (w), 2720 (w), 1595 (m), 1488 (m), 1020 (m), 764 (m), 700 (s) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2\overline{TiOC(O)CH_2CH_2}$ (22). Carbon dioxide (1.07 mmol) was added to a stirred solutionof 1 (360 mg, 1.04 mmol) in 10 mL toluene at -78°. The reaction was allowed to proceed 15 min at -78° then the mixture was warmed to 25°. The toluene and excess $CO_2$ were removed under vacuum and the resulting red solid was recrystallized from cold petroleum ether to give 325 mg (80%) pure 22. IR: 1663 (vs), 1277 (s), 1250 (s), 1219 (m), 1020 (m), 895 (s), 860 (m), 421 (s), 380 (s) $cm^{-1}$.

$(\eta\text{-}C_5Me_5)_2\overline{TiOCH(CH_3)CH_2CH_2}$ (23). Following the same procedure as that used for 22, the red-orange, very soluble 23 was isolated in 31% yield. IR: 2722 (w), 1363 (m), 1320 (m), 1217 (m), 1115 (m), 1080 (s), 1020 (m), 1002 (m), 903 (s), 830 (m), 582 (s) $cm^{-1}$.

Carbonylation of 12. Benzene-$d_6$ (0.5 mL) was condensed at -196° into a thick-walled glass vessel containing 1 (45 mg, 0.13 mmol). Carbon monoxide (10 mmol) was added and the contents were heated and stirred at 80° for 48 h. The excess CO was removed by three freeze-pump-thaw cycles at -196°, then the benzene-$d_6$ and any volatiles were vacuum transferred at 25° into an NMR tube and found to contain a trace of 2,3-dimethyl-2-cyclopentenone. The contents of the glass vessel were identified as $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$[4] and 2,3-dimethyl-2-cyclopentenone by $^1H$ NMR and IR.[5]

Table IV. Elemental Analysis and Molecular Weight Data

| Compound | | %C Calcd;Found | %H Calcd;Found | %Ti Calcd;Found | Mol Wt Calcd;Found |
|---|---|---|---|---|---|
| $(C_5Me_5)_2\overline{TiN=C(CH_2CH_3)CH_2CH_2}$ | 4 | 74.79 74.64 | 9.79 9.85 | 11.93 12.05<br>3.49[a] 3.31[a] | 401 390 |
| $(C_5Me_5)_2\overline{TiN=C(CMe_3)CH_2CH_2}$ | 5 | 75.50 74.84 | 10.09 9.97 | 11.15 11.30<br>3.26[a] 3.52[a] | |
| $(C_5Me_5)_2\overline{TiN=C(C_6H_4CH_3)CH_2CH_2}$ | 6 | 77.73 77.64 | 8.92 8.70 | 3.02[a] 3.21[a] | 464 439 |
| $(C_5Me_5)_2\overline{TiCH=C(CH_3)CH_2CH_2}$ | 8 | 77.70 77.15 | 9.91 9.87 | 12.39 12.66 | 386 384 |
| $(C_5Me_5)_2\overline{TiC(CH_3)=C(CH_3)CH_2CH_2}$ | 12 | 77.97 77.75 | 10.07 9.94 | 11.96 11.85 | 401 386 |
| $(C_5Me_5)_2Ti(C_6H_5C{\equiv}CC_6H_5)$ | 14 | 82.23 81.93 | 8.12 8.02 | 9.65 9.90 | 495 463 |
| $(C_5Me_5)_2\overline{TiOC(O)CH_2CH_2}$ | 22 | 70.76 70.31 | 8.78 8.81 | 12.27 12.15 | 390 386 |
| $(C_5Me_5)_2\overline{TiOCH(CH_3)CH_2CH_2}$ | 23 | 73.83 73.40 | 9.81 9.93 | 12.27 12.79 | |

[a] %N

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# Chapter III

## Molecular Dynamics and Reactivity of Bis Pentamethylcyclopentadienyl Niobium Tetrahydroborate

## Introduction

Bis(cyclopentadienyl)niobium compounds exhibit diverse and interesting chemistry.[1-7] Four formal oxidation states, II, III, IV, and V, have been observed for the niobium in this class of compounds. In addition to uncharged, diamagnetic complexes, cationic and anionic derivatives are readily prepared, as are paramagnetic species. A particularly reactive niobocene species is the trihydride complex, $Cp_2NbH_3$ (1).[1] Formally a nine-coordinate, eighteen-electron, $d^0$ species, 1 has been found to effect hydrogen-deuterium exchange between $H_2$ and $C_6D_6$,[1a,c] catalyze the hydrogenation of ethylene,[1a] and reduce carbon monoxide under dihydrogen to small amounts of methane.[7] It also serves as the precursor for a large number of derivatives; e.g., the first isolable example of a cis hydride olefin complex,[1a,3] Lewis acid adducts,[1b] an oxycarbene hydride species which undergoes reversible hydrogen migration $\rightleftharpoons$ $\alpha$-hydrogen abstraction,[6] numerous hetero-metallic dimers,[7,8] and compounds of the type, $Cp_2NbH(L)$, where L = CO, phosphine, alkyne, etc.[1,5] In the absence of a suitable substrate, 1 releases 1.5 mol $H_2$/mol 1 and yields dimeric "niobocene",

$$2Cp_2NbH_3 \rightarrow [CpNbH(C_5H_4)]_2 + 3H_2 \qquad (1)$$

$[CpNbH(\mu\text{-}C_5H_4)]_2$ (2).[1a,9]

Much of the reactivity of 1 has been attributed to the initial formation of a postulated intermediate, $Cp_2NbH$ (A), as shown in eq. 2.[1a,c] The tendency of 1 to form the very stable niobocene dimer 2, however, has thus far prevented the observation of A. Another

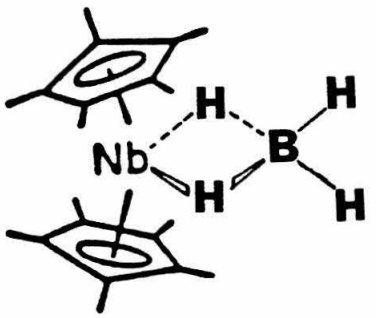
$$Cp_2NbH_3 \rightleftharpoons [Cp_2NbH] + H_2 \qquad (2)$$

$$\underset{\sim}{1} \qquad\qquad \underset{\sim}{A}$$

consequence of reaction 1 is the deactivation of the niobium center towards further reaction. Since the formation of dimeric and oligomeric complexes of titanium and zirconium is suppressed by the use of pentamethylcyclopentadienyl ligands in place of the $C_5H_5$ ligands,[10] an investigation of bis(pentamethylcyclopentadienyl)niobium compounds was undertaken, the results of which are reported below.

Results and Discussion

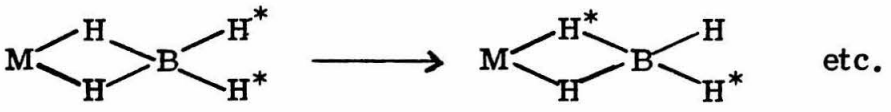
Entry into the chemistry of $(\eta\text{-}C_5Me_5)_2Nb$ complexes has been made available with the preparation of bis(pentamethylcyclopentadienyl)niobium tetrahydroborate, $(\eta\text{-}C_5Me_5)_2NbBH_4$ (3). The tetrahydroborate compound is obtained from the reaction of $NbCl_5$ with excess $LiC_5Me_5$ and $NaBH_4$ in dimethyoxyethane in 30-40% yield. The green, air-sensitive 3 exhibits an infrared spectrum character-




3

istic of bidentate coordination of the $BH_4^-$ ligand:[11] $B\text{-}H_t$ = 2452, 2428; $B\text{-}H_b$ = 1728, 1620; $BH_2$ def. = 1171 $cm^{-1}$. The $^1H$ NMR spectrum of 3 consists of a sharp singlet at $\delta$ 1.67 and two very broad resonances at $\delta$ 5.2 and -18.2 in the ratio 30.6:2.3:2.0, respectively.

One property of transition metal tetrahydroborate compounds is the rapid intramolecular exchange between the terminal and bridging hydrogens of the tetrahydroborate:

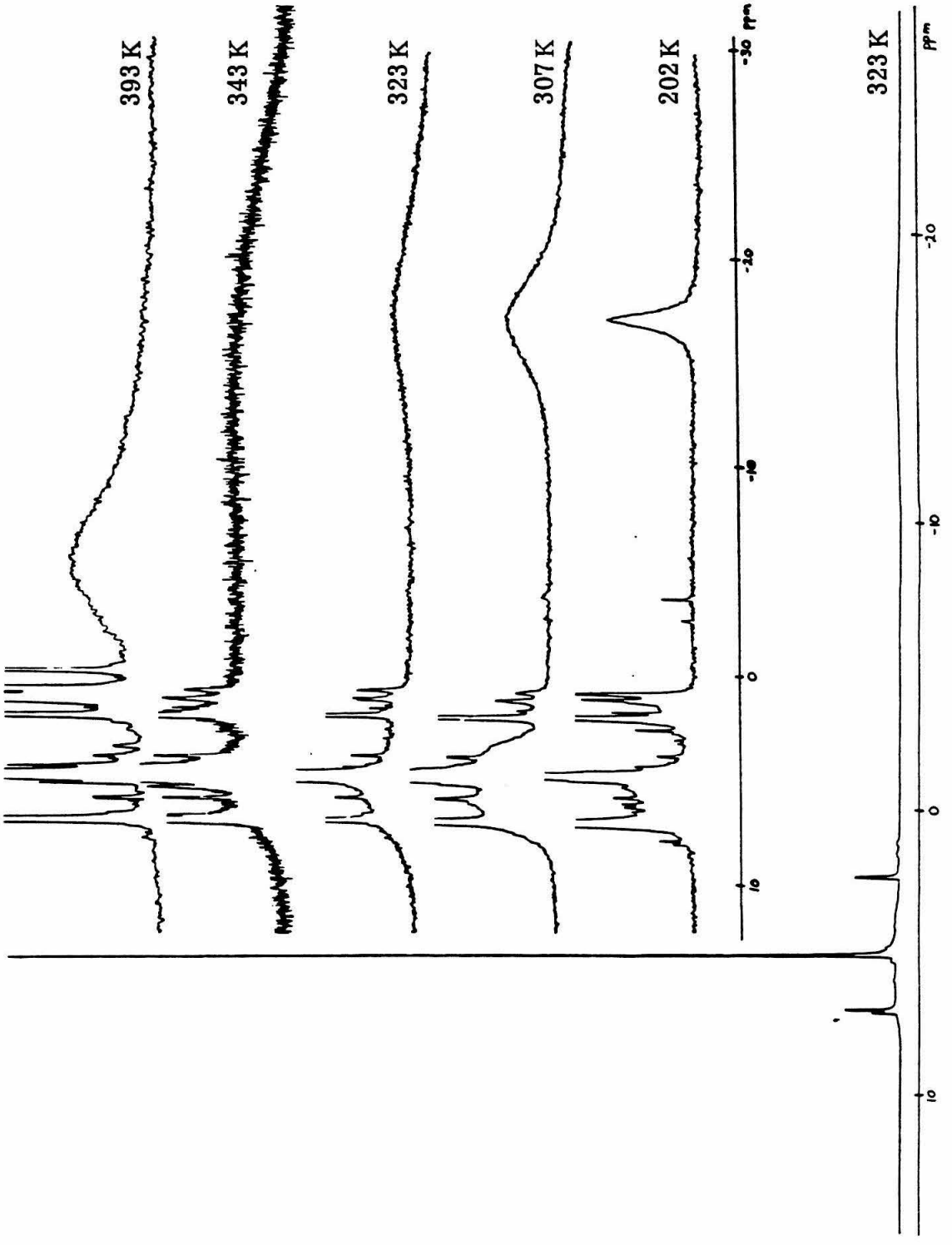



Even at low temperatures, this exchange process has been slowed or stopped in very few compounds on the time scale of the NMR experiment. Based on the temperatures required, very low energies of activation for the averaging processes ($\leq$ 11 kcal $\cdot$ mol$^{-1}$) have been found.[11,12]

Observation of the broad resonances at $\delta$ 5.2 and -18.2 at ambient temperatures prompted a variable temperature NMR study of $\underset{\sim}{3}$ (Fig. 1). Lowering the temperature of the sample from 283° K decreases the spin-lattic relaxation time, $T_1$, of the boron nuclei, effectively decoupling the boron with respect to the protons.[13] This thermal decoupling is reflected in the coalescence of the doublet of terminal hydrogens[14,15] and the further narrowing of both the $H_t$ and $H_b$ resonances. At 283° K, $^1$H lineshapes are dominated by spin-coupling to the $^{11}$B (S = $\frac{3}{2}$, 80.22% abundance), the narrower $H_b$ singlet being consistent with the smaller coupling constant expected for the bridging hydrogens ($J_{B-H_b} \simeq 50$ Hz) as compared with that predicted for the terminal hydrogens ($J_{B-H_t} \simeq 130$ Hz).[16] Above 307° K the resonances broaden and shift towards each other as $H_b$-$H_t$ exchange begins.[17] Coalescence is observed at 388 $\pm$ 8° K; some sharpening of the averaged resonance at ca. $\delta$ -7 is detected at 403° K. The free energy of activation for the exchange process ($\Delta G^{\ddagger}$) in $\underset{\sim}{3}$ is 16.4 $\pm$ 0.4 kcal $\cdot$ mol$^{-1}$.[18,19]

The low temperature $^1$H NMR spectrum of $Cp_2NbH_4$ ($\underset{\sim}{4}$) is reported

Figure 1. Variable temperature $^1H$ NMR spectra of $\underset{\sim}{3}$ in $C_7D_8$. Samples contain traces of $(\eta\text{-}C_5H_5)_2NbH_3$ and petroleum ether. Sample for 393° K contains TMS.


393 K
343 K
323 K
307 K
202 K
323 K
ppm

to be a sharp singlet at $\tau$ 4.93 and a single broad resonance at $\tau$ 26.2 ($\delta$ -16.2), which are assigned to the $C_5\underline{H}_5$ ligand and the four magnetically averaged hydrogens of the $BH_4^-$ ligand, respectively.[11b] Based on these data, the activation energy ($E_a$) for $H_b$-$H_t$ averaging in $(C_5H_5)_2NbBH_4$ is calculated to be $\leq 5.6$ kcal $\cdot$ mol$^{-1}$. One would not have predicted great differences in behavior between $\underset{\frown}{3}$ and $\underset{\frown}{4}$, particularly based on their nearly identical infrared spectra. The proximity of the "$BH_4^-$" resonance reported for $\underset{\frown}{4}$ to the $H_b$ resonance in $\underset{\frown}{3}$, the similar IR data, and the possibility that the $C_5H_5$ resonance of $\underset{\frown}{4}$ may obscure the $H_t$ resonance in the slow exchange limit suggested the reinvestigation of $\underset{\frown}{4}$. The 90 MHz proton NMR spectrum of $\underset{\frown}{4}$ was recorded at 313° K in benzene-$d_6$ (TMS): integration of the $C_5H_5$ region and the region ca. $\delta$-16 gives a ratio of 12.6 : 2.0, after correcting for the residual $C_6D_5H$,[20] in agreement with the calculated ratio of 12 : 2 expected if the $C_5H_5$ and $H_t$ resonances are nearly coincident. The 13.6 MHz $^2$H NMR spectrum of $(\eta$-$C_5H_5)_2NbBD_4$ ($\underset{\frown}{4}$-$\underline{d}_4$) is shown in Fig. 2: two broad peaks at $\delta$ 5.7 and -16.5 ($D_t$ and $D_b$, respectively) are observed along with the sharper $C_6H_5D$ and $C_5D_xH_{5-x}$ resonances. These data clearly establish that the room temperature proton NMR spectra for $\underset{\frown}{3}$ and $\underset{\frown}{4}$ are similar and consistent with the static bidentate structures indicated by the infrared data.

The variable temperature $^1$H NMR spectra of $\underset{\frown}{4}$ were recorded between 202° and 393° K in toluene-$d_8$ solution (Fig. 3). The $H_t$ and $H_b$ resonances of $\underset{\frown}{4}$ at $\delta$ 5.7 and -16.5, respectively, narrow upon cooling below 300° K. Coalescence is observed at 346 ± 3° K; at 393° K, a single broad peak centered at ca. $\delta$ -5.4 is seen. From the observed

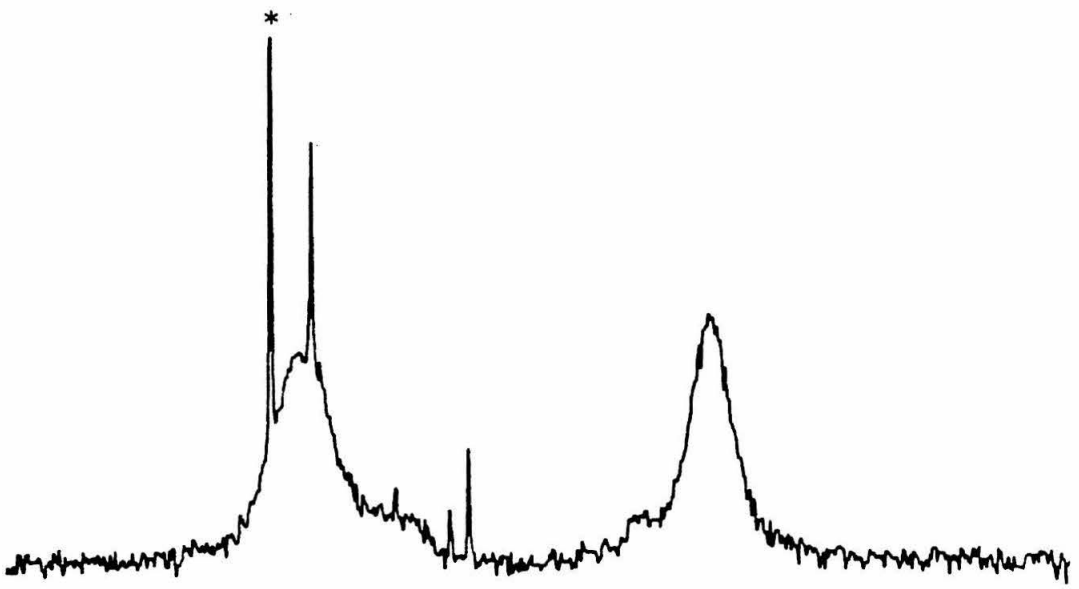



Figure 2. $^{2}H$ NMR spectrum (13.7 MHz) of $(\eta\text{-}C_5H_5)_2NbBD_4$ in $C_6H_6$ (34°). Starred resonance is natural abundance $C_6H_5D$. Sample also contains a trace of $(\eta\text{-}C_5H_5)_2NbD_3$.

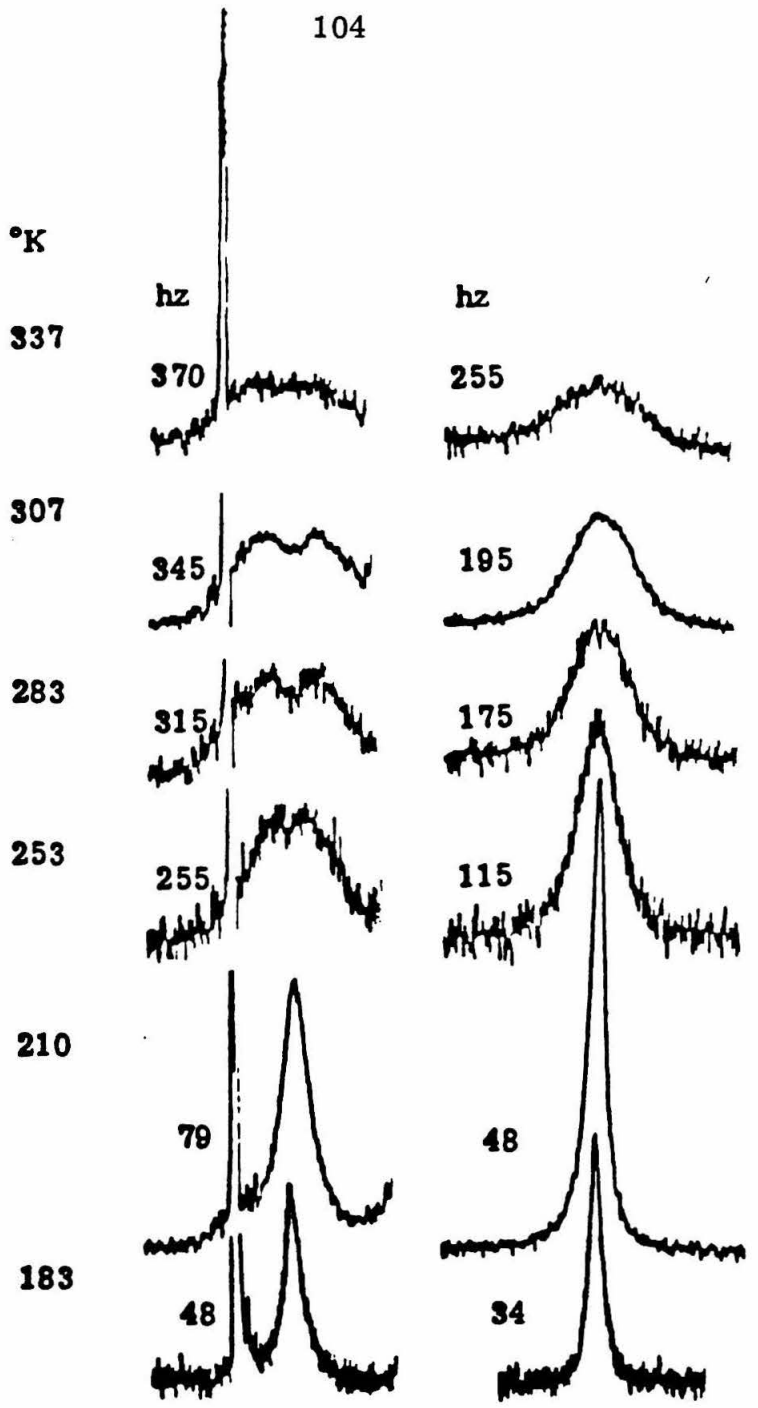



Figure 1. 90 MHz $^1$H NMR spectra of $\underset{\sim}{3}$ (50 ppm sweep width) for terminal (left) and bridging (right) hydrogen resonances between 183° and 337° K. Numbers to the immediate left of the peaks are full-width-at-half-maximum-height values; sharp peak near terminal hydrogen resonance is due to residual $CD_3C_6D_4H$.

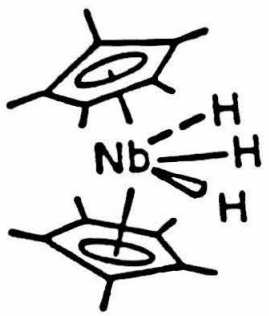
coalescence temperature and a low temperature peak separation ($\Delta\nu$) of 1970 ± 30 Hz, a free energy of activation, $\Delta G^{\ddagger} = 14.6 \pm 0.2$ kcal · mol$^{-1}$ is calculated for the $H_b$-$H_t$ averaging process in 4. This value compares favorably with the $\Delta G^{\ddagger}$ of 16.4 ± 0.4 kcal · mol$^{-1}$ found for 3; the difference suggests a slightly stronger Nb-$H_2$-$BH_2$ interaction in 3 than in 4 and is consistent with the IR data.

Treatment of $(\eta\text{-}C_5Me_5)_2NbBH_4$ (3) with pyridine and $H_2$ in toluene affords $(\eta\text{-}C_5Me_5)_2NbH_3$ (5) in high yield. Repeated recrystallizations

$$(C_5Me_5)_2NbBH_4 + C_5H_5N + H_2 \rightarrow (C_5Me_5)_2NbH_3 + C_5H_5N{:}BH_3 \qquad (3)$$

3 5

under ca. 700 torr $H_2$ from octane and light petroleum ether are necessary to isolate the white crystalline compound free of all highly colored impurities. The $^1$H NMR spectrum of 5 shows a singlet at δ 1.81 and a broad doublet at -2.31 (J = 3 Hz) which is coupled to a very broad resonance at -1.23; these correspond to the $C_5Me_5$ hydrogens, the outer




5

hydrides, and the central hydride, respectively. In the absence of dihydrogen, solutions of 5 are unstable, similar to $Cp_2NbH_3$ (1), although NMR samples prepared in sealed tubes without added $H_2$ are stable indefinitely at 25 . When such a sample is heated at 75 , the colorless solution of 6 becomes increasingly yellow as a new singlet grows in the NMR spectrum at δ 1.61. After 40 minutes its integrated intensity maximizes at 15% of the intensity for the ring methyl resonance of 5 at δ 1.81. Formation of this species is reversible in a closed system, the yellow color and the singlet at δ 1.61 disappear after 6-10 weeks at 25° and reappear with resumed heating. The formation of this species is suppressed by the presence of 1 atm $H_2$, the maximum integrated intensity in the NMR being 7% (versus 5) after 4 hours at 78°. No H-D exchange between 5 and $C_6D_6$ is observed in the sample after days at 80°. Attempts to generate higher concentrates of the yellow species by thermolysis of 5 at 80° with removal of the liberated dihydrogen by Toepler pump lead instead to very deep green solutions which contain at least two paramagnetic niobium complexes, based on EPR spectral evidence.[21] The behavior of the yellow species suggests that it may be the monohydride complex, $(\eta\text{-}C_5Me_5)_2NbH$ (6); however, other structures cannot be excluded.

Excess ethylene reacts with $(\eta\text{-}C_5Me_5)_2NbH_3$ in toluene or benzene solution at 85° C to yield green-yellow $(\eta\text{-}C_5Me_5)_2NbH(\eta\text{-}C_2H_4)$ (7) (98% by NMR). Besides the $C_5(CH_3)_5$ singlet at δ 1.64, the $^1H$ NMR spectrum of 7 consists of the broad hydride singlet at δ 2.99 and an AA'BB' pattern for the inequivalent ends of the ethylene: the two complex triplets centered about δ +0.65 and δ -0.25 are very similar to the $^1H$

NMR spectra reported for $Cp_2NbH(\eta\text{-}C_2H_4)$ and $Cp_2Nb(C_2H_5)(\eta\text{-}C_2H_4)$.[3a]

$$(C_5Me_5)_2NbH_3 + C_2H_4 \rightarrow (C_5Me_5)_2NbH(C_2H_4) + H_2 \qquad (4)$$
$$\underset{\sim}{5} \qquad\qquad \underset{\sim}{7}$$

Further investigation of the reaction of $\underset{\sim}{5}$ with ethylene (eq. 4) uncovered the slow production of ethane (ca. 0.1 mol $C_2H_6$/mol $\underset{\sim}{7}$ after 4 h). The hydrogenation of excess ethylene continues until the dissolved $H_2$ is exhausted. The reaction of $\underset{\sim}{7}$ with excess $H_2$ also occurs (eq. 5), thus enabling $\underset{\sim}{5}$ and/or $\underset{\sim}{7}$ to slowly catalyze the hydrogenation of

$$(C_5Me_5)_2NbH(C_2H_4) + 2H_2 \rightarrow (C_5Me_5)_2NbH_3 + C_2H_6 \qquad (5)$$
$$\underset{\sim}{7} \qquad\qquad \underset{\sim}{5}$$

ethylene.

The trihydride $\underset{\sim}{5}$ reacts with carbon monoxide at elevated temperatures to produce the carbonyl hydride complex, $(\eta\text{-}C_5Me_5)_2NbH(CO)$ ($\underset{\sim}{8}$).

$$(C_5Me_5)_2NbH_3 + CO \rightarrow (C_5Me_5)_2NbH(CO) + H_2 \qquad (6)$$
$$\underset{\sim}{5} \qquad\qquad \underset{\sim}{8}$$

The carbonyl hydride complex has been characterized by IR ($\nu_{CO}$ = 1865; $\nu_{Nb\text{-}H}$ = 1700 $cm^{-1}$) and NMR spectroscopy (Nb-$\underline{H}$, $\delta$ -5.6) as well as elemental analysis. Like the parent $Cp_2NbH(CO)$ complex, $\underset{\sim}{8}$ is found to be unreactive toward several atmospheres of $H_2$ or excess $C_2H_4$.

The dichloride compound $(\eta\text{-}C_5Me_5)_2NbCl_2$ ($\underset{\sim}{9}$), can be prepared in good yield by the reaction of $(\eta\text{-}C_5Me_5)_2NbBH_4$ with aqueous, deoxygenated HCl. Paramagnetic $\underset{\sim}{9}$ exhibits a ten-line EPR spectrum ($^{93}$Nb I = 9/2) and has a magnetic moment of 1.91 BM. Reduction of the

dichloride with Na/Hg under an atmosphere of hydrogen affords a mixture of the trihydride 5 and the corresponding dihydride $(\eta\text{-}C_5Me_5)_2NbH_2$ (10), as identified by its EPR spectrum.

The preparation of other derivatives as well as studies related to the mechanisms of some of the reactions described are currently underway.[22]

Experimental

Synthesis and manipulation of compounds were carried out using high vacuum/inert atmosphere techniques. Argon, dinitrogen, dihydrogen, and dideuterium (Matheson, 98.7% $D_2$) were purified by passage over MnO on vermiculite, followed by 4 Å molecular sieves. Toluene, benzene, petroleum ether (35°-60°), and octane were dried over $LiAlH_4$ and then vacuum transferred from titanocene. Pyridine was dried and vacuum transferred from $CaH_2$. Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl. Methylene chloride was distilled in vacuo from molecular sieves. Ethylene was collected at -196°, freeze-pump-thaw degassed, and vacuum transferred at -78°. Carbon monoxide (MCB) was used without purification. Normal $Cp_2NbBH_4$ and $Cp_2NbBD_4$ were prepared by literature methods,[23] the latter using $NaBD_4$ (Stohler, 99% D). Lithium pentamethylcyclopentadienide was prepared by literature methods.[24] Niobium pentachloride was initially sublimed at 110° ($10^{-4}$ torr) to remove most of the $NbOCl_3$, followed by one or more sublimations at $< 100°$ ($10^{-4}$ torr) which yielded $NbCl_5$ having no Nb-O stretches in the IR.

Infrared spectra were recorded as Nujol mulls on a Beckman 4240 spectrophotometer. Nuclear magnetic resonance spectra were recorded on Varian EM-390 and JEOL FX90Q spectrometers. EPR spectra were measured on an X-band Varian E-line Century Series spectrometer. Magnetic susceptibilities were determined using a Cahn/Ventron susceptibility balance. Benzene-$\underline{d}_6$ (Aldrich, 99.5% D) and toluene-$\underline{d}_8$ (Stohler, 99.5% D) were dried over molecular sieves and vacuum transferred from titanocene.

Procedures ($\eta$-$C_5Me_5)_2NbBH_4$ (3). Pentamethylcyclopentadiene (21.3 g) was syringed into a one liter flask cooled to -78° containing $LiCH_2CH_2CH_2CH_3$ (158 mmol) in DME (250 mL). The mixture was allowed to warm to 25°. After stirring 3 h at 25°, the suspension of $LiC_5Me_5$ was cooled to -78°, $NaBH_4$ (21.4 g) was added, and $NbCl_5$ (17.7 g, 65.6 mmol) was slowly added over a 3 h period while stirring. The resulting brown mixture was allowed to warm to 25°, then heated to reflux for five days. Volatiles were removed in vacuo and the purple solid was sublimed at 120°. The green sublimate was recrystallized from petroleum ether, affording 8.8 g of 3 (36%). IR: 2716 (w), 2452 (s), 2428 (s), 2312 (m), 1728 (w), 1620 (m), 1516 (m), 1483 (s), 1417 (m), 1390 (w), 1171 (s), 1028 (s), 864 (s), 798 (w), 420 (m). NMR: 1.67 (s), 5.2 (br), -18.2 (br). Anal. Calcd. for $C_{20}H_{34}BNb$: C, 63.52; H, 9.06; B, 2.86; Nb, 24.56. Found: C, 63.36; H, 8.96; B, 2.92; Nb, 25.04. Mass spec: parent m/e 378.178 (calc. 378.181). Melting point: 239-241° (slight dec.).

($\eta$-$C_5Me_5)_2NbH_3$ (5). Pyridine (15 mL) was added to a toluene solution (10 mL) of 3 (5.61 g, 14.8 mmol) at -196°. One atm $H_2$ was added as the solution was allowed to warm to room temperature and was stirred for 8 hours. The red solution was filtered and cooled to produce a light pink solid. The solid was washed with cold petroleum ether and dried under vacuum to yield 4.3 g (13.2 mmol) pink 5 (89%). Repeated recrystallizations from octane and petroleum ether under 1 atm $H_2$ gave the white, air-sensitive product in 78% yield. IR: 1752, 1697, 1027, 773 $cm^{-1}$. NMR: $\delta$ 1.81 (s), -1.23 (s,br), -2.31 (d, J = 3.6 Hz); integrated intensities, 30.7:1.00:1.95. Anal. Calcd. for $C_{20}H_{33}Nb$:

C, 65.56; H, 9.08; Nb, 23.36. Found: C, 64.92; H, 9.29; Nb, 25.07.

$(\eta\text{-}C_5Me_5)_2NbH(\eta\text{-}C_2H_4)$ (7). A 25 ml flask was charged with 5 (1.17 g, 3.19 mmol) and attached to a frit assembly. Toluene (5 mL) and excess $C_2H_4$ were condensed onto the solid at -196°. The mixture was warmed to 85° and stirred 11 h. The brown solution was cooled to 0°, affording yellow-green crystals of 7 which were collected on the frit. The filtrate was frozen in a -196° bath and the residual gas was collected via a Toepler pump and burned, indicating 0.33 mol $H_2$/mol 5 remained. The solid was recrystallized from toluene and washed with petroleum ether yielding 0.73 g 7 (58%). IR: 3051 (w), 1707 (m), 1131 (s), 1024 (s) $cm^{-1}$. NMR: δ 1.64 (s), 0.65 (t, J = 10.5 Hz), -0.25 (t, J = 10.5 Hz), -2.99 (s); integrated intensities 29.4 : 2.0 : 2.0 : 0.8. Anal. Calcd. for $C_{22}H_{35}Nb$: C, 67.73; H, 9.16. Found: C, 67.34; H, 8.99.

Formation of 7 and $C_2H_6$ is >98% by NMR, based on starting material (5).

$(\eta\text{-}C_5Me_5)_2NbH(CO)$ (8). A toluene solution (25 mL) of 5 (1.2 g) was heated to 95° under an atmosphere of CO for 16 h. The volatiles were removed in vacuo and the residue was recrystallized from cold octane, yielding 1.1 g 8 (90%). IR: 2730 (w), 1865 (s), 1700 (m), 1031 (s), 480 (m). NMR: δ 1.80 (s), -5.6 (s, br); 30 : 1. Anal. Calcd. for $C_{21}H_{31}NbO$: C, 64.28; H, 7.96; Nb, 23.68. Found: C, 64.13; H, 8.06; Nb, 23.90.

$(\eta\text{-}C_5Me_5)_2NbCl_2$ (9). Deoxygenated 3 M aqueous HCl (15 mL) was reacted with 3 (5.3 g) in 100 mL benzene at 5°. Gases were vigorously

evolved and a yellow precipitate formed in the brown solution which was stirred 20 min. Volatile components were removed in vacuo and the brown residue was extracted with benzene. The brown microcrystalline product was dissolved in $CH_2Cl_2$ (120 mL), 0.5 g degassed grade III alumina was added and the mixture was filtered. The filtrate was stripped of solvent and the resulting solid was recrystallized from toluene, affording 4.1 g 9 (67%). EPR (benzene): ten-line spectrum, g = 2.01. Magnetic susceptibility: 1.91 BM. IR: 2720 (w), 1165 (w), 1065 (m), 1020 (s), 847 (s), 806 (w), 412 (w), 376 (s). Anal. Calcd. for $C_{20}H_{30}Cl_2Nb$: C, 55.31; H, 6.96; Cl, 16.33; Nb, 21.39. Found: C, 55.41; H, 7.03; Cl, 16.29; Nb, 21.52.

Reduction of 9 under $H_2$. A benzene slurry of 9 (0.97 g in 100 mL) was stirred with excess Na amalgam (1%) under 1 atm hydrogen for one day. The resulting red solution was decanted from the amalgam and filtered. The benzene was removed in vacuo and the red solid was recrystallized under $H_2$. Yield was ca. 600 mg of a mixture containing $(\eta\text{-}C_5Me_5)_2NbH_2$ (EPR, ten-line spectrum, g = 2.01) and 5.

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18. $k_c = \pi(\Delta\nu)/\sqrt{2} = (kT/h)\exp(-\Delta G^{\ddagger}/RT)$, where $k_c$ is the rate at coalescence, $\Delta\nu$ is the energy separation between the peaks in the slow exchange limit (Hz), T is the temperature (°K), and k, h, and R are Boltzmann's constant, Planck's constant, and the gas constant, respectively. See H. Kessler, Angew. Chem. Int. Ed. Eng. 9, 219 (1970).

19. For 3, $\Delta\nu = 2090 \pm 30$ Hz, and $T = 388 \pm 5$°K.

20. It was found that very low r.f. power settings are necessary to avoid saturation of the ring proton resonances for both 3 and 4. Integration for 3 at a typical r.f. power of 0.10 mG yields $H_t : H_{ring} : H_b$ of 2.1 : 14.8 : 2.0 (calc. 2 : 30 : 2) whereas at r.f. power = 0.04 mG, the ratios are 2.3 : 30.6 : 2.0. Similar results were obtained for 4 and may explain the results reported in Ref. 11b.

21. The room temperature EPR spectrum of the deep-green solution shows a major species having an unstructured ten-line pattern ($^{93}$Nb, I = 9/2) with g = 2.025 and a much weaker signal overlapping with the strong signal.

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17. The ring hydrogen resonance remains sharp throughout the experiment and all spectral changes observed for the $BH_4^-$ resonances are reversible.

# Abstracts of Propositions

Steven Alan Cohen

Proposition 1. An Electron Energy Loss spectroscopic investigation of the interaction of carbon monoxide adsorbed onto clean, single crystal surfaces of uranium is outlined.

Proposition 2. The hydrogenation of benzene to cyclohexane and cyclohexene using polystyrene-supported ruthenium catalysts is discussed.

Proposition 3. The investigation of the geometry and stability of chemisorbed sulfur dioxide on a clean vanadium surface is proposed.

Proposition 4. Synthesis and mechanistic studies involving tetrahapto-cyclopentadiene niobium complexes and their isomerization to pentahapto-cyclopentadienyl hydride species are discussed.

Proposition 5. The investigation of the synthesis and reactivity of organochromium (III) and (IV) compounds is proposed.

# PROPOSITION 1

The adsorption of carbon monoxide on single crystal surfaces of nearly every transition metal has been studied due to the importance of CO adsorption in gaining a general understanding of surface-adlayer interactions and the specific processes which may occur on heterogeneous catalyst sites.[1] Despite the intensive research, studies of actinide surfaces appears to have been completely ignored. A study of the adsorption of carbon monoxide on single crystal surfaces of uranium by Electron Energy Loss Spectroscopy is proposed.

Vibrational spectroscopy has long been used to characterize the structure and bonding of chemical species. Only recently, however, have methods been developed for obtaining vibrational information of species adsorbed on well defined single crystal surfaces. High Resolution Electron Energy Loss Spectroscopy (EELS), and Infrared Reflection Spectroscopy (IRS) are the most useful of these techniques. Although experimentally very different, both EELS and IRS operate by the same physical process - the absorption of energy by a vibrating dipole with a component normal to the plane of the surface.[2] Currently, EELS suffers from poorer resolution than IRS (by a factor of 10), but has much greater sensitivity than IRS (by a factor of 50).[3] In addition, Electron Energy Loss spectrometers have been successfully incorporated into conventional ultra-high vacuum systems containing LEED, Auger, Mass Spectroscopy, and other surface characterization techniques, allowing more complete analyses of adsorbate-substrate systems. Due in part to EELS's high sensitivity, EELS spectroscopic data have

provided evidence for a number of surface phenomena; dissociative and non-dissociative adsorption, specific site preference, adlayer geometry with respect to the surface, mechanistic pathways for surface reactions, and the existence of reaction intermediates.

A brief discussion of the experimental aspects of EELS is necessary before treating individual adsorbate-substrate systems. Electron Loss Spectroscopy has the same selection rule as Infrared Reflection Spectroscopy; a vibrational motion which produces a change in the dipole moment having a component perpendicular to the plane of the surface is "allowed". Experimentally, however, EELS is more aptly described as an analogue of Stokes Raman Spectroscopy (SRS). The SR effect is observed as the inelastic scattering monochromatic photons, initial energy $E_0$ and final (lower) energy $E_1$, where the difference $E_0 - E_1$ is the energy corresponding to a particular molecular vibration $h\nu$. Monoenergetic electrons (instead of photons) are employed in the EELS experiment and again the energy differences between the elastically and inelastically scattered electrons correspond to molecular vibrational modes. Extending the analogy further, one might predict an effect similar to Anti-Stokes Raman Scattering and indeed electron energy gain has been observed.[4] The existence of a resonance enhancement condition for electron scattering, comparable to the Resonance Raman effect, has also been indicated.[5] Finally, it might be noted that overtone and combination bands are present in EEL spectra just as they are in Infrared and Raman spectra.[6,7]

An Electron Energy Loss spectrometer is schematically represented in the Figure.

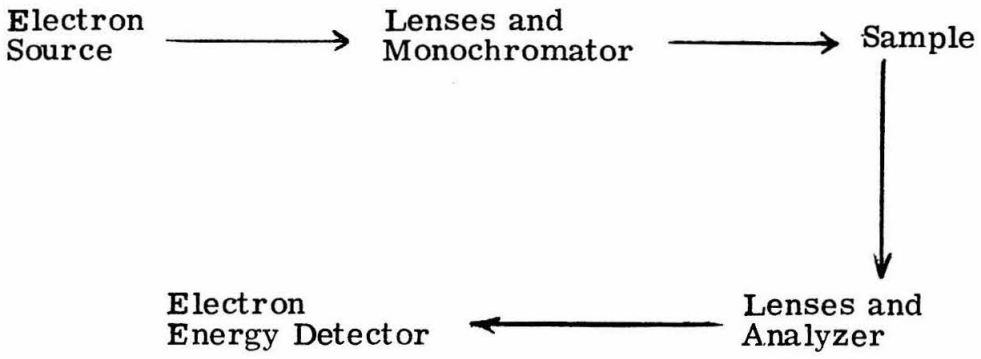


Figure.

The qualitative similarity between the instrumentation used for electron and photon scattering experiments (EELS and Raman, respectively) is quite apparent since a Raman apparatus also consists of a (photon) source, lens, sample, analyzer and detector. The geometric configurations of EELS instruments differentiate them as one of three types: 120-127° sector analyzer, cylindrical mirror analyzer, and 180° hemispherical analyzer. The characteristics of each type of instrument have been discussed recently,[3] but it should be noted that a 180° hemispherical model has been developed[7] which has comparable resolution to other spectrometers (full width at half maximum height of the elastically scattered peak is 7 to 10 meV = 55 to 80 $cm^{-1}$) and is more versatile with regard to doing both off-specular studies and experiments involving higher energy electrons ($10^1$ to $10^3$ eV). The development of higher resolution instruments should continue to be an active area of research. Improved resolution would allow better characterization of surface species with more accurate spectral assignments and inter-

pretation of data, primarily from the more routine application of isotopic labeling techniques as a means of identifying specific vibrational modes. Mechanistic studies of surface reactions, an area of increasing activity, require these labeling techniques in all but the simplest cases and even then, results must be interpreted with great care.

The EEL spectra of adsorbed carbon monoxide may be obtained over a wide range of surface coverages due to the strong $\nu$(CO) band(s). Following the preparation and characterization[8] of the single crystal sample of uranium, initial experiments involving the exposure of the surface to varying coverages of carbon monoxide at ambient temperature would establish whether the adsorption process is associative or dissociative. Metallic uranium readily forms very stable oxides and carbide complexes,[9] suggesting that such dissociative reactivity will occur prior to desorption of the admolecules from the surface. The pre-dissociative interactions may be observed by performing the reactions at low temperatures (i.e., 100° K), if necessary.[10] The presence of a CO stretch, typically above 1700 $cm^{-1}$, distinguishes associative from dissociative adsorption. Metal-carbon stretches can also be observed and would be used to establish whether the coordination of the CO to the uranium occurs via the carbon. These data could be compared with those obtained from uranium carbonyls under matrix isolation conditions.[11] Dissociative adsorption of CO on U could be characterized by loss of the $\nu$(CO) feature while stretches in the low energy region (>1000 $cm^{-1}$) increase , corresponding to the formation of surface oxides and carbons.[12] Finally, heating of the sample to effect desorption would be monitored by mass spectroscopy and, in conjunction with the use of labelled carbon monoxide, atomic scrambling

processes could be monitored.

A great deal can be learned about the surface chemistry of uranium from the study of adsorbed carbon monoxide by Electron Energy Loss Spectroscopy. The results from these experiments will serve as an indicator for further work. Prior oxidation of the surface and exposure of the CO/U samples to $H_2$ or $H_2O$ are likely "second generation" experiments and could uncover interesting chemical reactivity.

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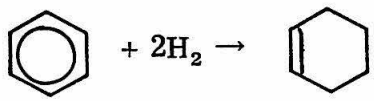
## PROPOSITION 2

The attachment of transition metal complexes to insoluble supports has received considerable attention as a method of combining the desirable properties of homogeneous catalysis with those of heterogeneous catalysis.[1] Hybrid catalysts offer the selectivity, specificity, reproducibility, control of composition, and efficiency of homogeneous compounds with the ease of catalyst separation inherent in heterogeneous processes.

One method for preparing hybrid catalysts which has had limited success is the copolymerization of an organic monomer such as methylacrylate or styrene with a monomer containing a metal species (e.g., ($\eta^6$-styrene)$Cr(CO)_3$,[2] vinyl ferrocene,[2] or (p-vinylphenyl)$Pt(PBu_3)_2Cl$).[3] More commonly, however, polyvinylpyridine[4] and functionalized polystyrene are treated with metal compounds having one or more labile ligands to form the desired metal-polymer material. Modified polystyrenes having phosphines,[5] amines,[6] sulfur and oxygen donors,[6] nitriles,[6] and cyclopentadienyl[7] ligands have been prepared and studied extensively using a variety of metal complexes.

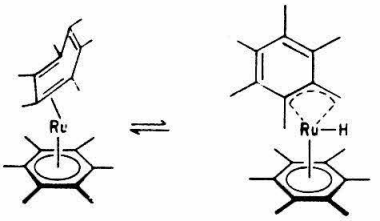
Use of the phenyl ring of unmodified polystyrene as the attaching ligand has not been widely explored.[2] The most promising data on the formation of metal $\pi$-arene surface species come from studies of metal film adhesion to polymer substrates. Investigating questions related to metal thin films for electronic and plating uses, Burkstrand has found a correlation between the shifts observed in the X-ray photoemission spectra of submonolayer coverages of copper, nickel, and chromium on

polystyrene and a $\pi$ interaction of the phenyl groups with the metal atoms.[8] Polymer-bound analogues of the eighteen electron compounds, bis(benzene)chromium, the formally twenty-two electron bis(benzene)-nickel, and the seventeen electron complex, ($\eta^6$-benzene)copper, have been postulated as discrete surface species. These results suggest that the use of the phenyl rings of polystyrene as ligands for supporting reactive metal complexes is a promising method of forming hybrid catalysts. Therefore the preparation of ($\pi$-arene)ruthenium derivatives of polystyrene and the investigation of their activity in catalyzing the hydrogenation of benzene are proposed. Interest in benzene hydrogenation stems from the importance of this reaction for the preparation of cyclohexane and the challenge of rationally developing catalysts for the specific hydrogenation of benzene to cyclohexene:[9a]



In comparison to the numerous homogeneous olefin hydrogenation catalysts which are known, very few compounds have been reported as homogeneous arene hydrogenation catalysts. Of the latter, nearly all decompose rapidly under reaction conditions.[9] A small number of rhodium and ruthenium complexes are found to be both active and long-lived catalysts, however. Both $(\eta^6\text{-}C_6Me_6)RuH(Cl)(PPh_3)$[10] and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2/NEt_3$[11] hydrogenate benzene exclusively to cyclohexane at 50° under 50 atm $H_2$, while $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H)_2(\mu\text{-}Cl)Ru(\eta^6\text{-}C_6Me_6)]Cl$ (I)[12] and $(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_4)Ru$ (II)[13,14] are notable for exhibiting a rapid turnover rate (4 $min^{-1}$) and the production of cyclohexene (ca. 5% vs.

cyclohexane), respectively. The hydrogenation of benzene by II has been postulated to occur via the hydridobenzylruthenium (II) isomer of II shown in the Figure.




Polystyrene derivatives of I and II would be prepared by a number of possible routes. Metal atom deposition[8] of Ru onto a polystyrene substrate (< one monolayer) followed by quenching with $C_6Me_6$ in hexane might lead to $(C_6Me_6)Ru(C_6H_5)$—Polymer. Alternatively, such a process could give surface species having one Ru bridging two phenyl rings of the polystyrene. Vapor deposition would limit the ruthenium to surface sites if no subsequent migration is observed. Permeation of the polystyrene with a solution of $(C_6Me_6)Ru(C_2H_4)_2$[12] followed by treatment with slightly greater than two equivalents of $H_2$ should produce a similarly derivatized polymer having internal as well as surface catalyst sites. Reduction of dichloride derivatives such as $[(C_6Me_6)RuCl_2]_2$[10] or the tris(acetonitrile)dication, $[(C_6Me_6)Ru(NCCH)_3](BF_4)_2$[15] in the presence of the polystyrene polymer might also afford the desired derivatives of II, $[(C_6Me_6)Ru(C_6H_5)]_x$—Polymer (III). Photolysis of a polystyrene sample which is permeated with a solution of

[p-$CH_3C_6H_4CH(CH_3)_2$]$RuCl_2(PBu_3)$ would be expected to displace the p-cymene ligand and yield the polymer-bound dichlorophosphine complex.[15] Treatment of the resulting polymer with excess $(C_6Me_6)RuCl(C_3H_5)$, followed by aqueous $NaCO_3$ and isopropanol[12] should give the heterogeneous analogue of I. $[(C_6Me_6)Ru(\mu\text{-}H)_2(\mu\text{-}Cl)Ru(C_6H_5)]_x$-Polystyrene (IV). Other synthetic routes involving $RuCl_3 \cdot xH_2O$ also could be employed.[13]

The coordination of the ruthenium species to $C_6H_5CH$ ligands rather than $C_6Me_6$ ligands could significantly alter the reactivity and/or stability of the hybrid catalysts vs. the homogeneous compounds. Moreover, since the rate of hydrogenation of toluene with I and II is only slightly slower than that of benzene, hydrogenation of the phenyl rings of the polystyrene support may be a problem. In accord with the observations that no ligand migrations or hydrogenations occur with highly substituted benzene ligands such as 1, 2, 3, 4-tetramethylbenzene or hexamethylbenzene,[10, 14a] the use of polymers made from methyl substituted styrenes may be required. Polymers of copolymers of four trimethylstyrenes[16] and 2, 3, 5, 6-tetramethylstyrene[17] are known and would offer a much closer approximation to the ligand environment in the homogeneous catalysts. Other factors which could also affect the preparation and activity of the catalysts include the extent of cross-linking within the polymer, surface area and pore size, catalyst concentration, migration and leaching of the catalytic species, the presence of ruthenium crystallites, and the stereoregularity of the polystyrenes used.[7, 9, 10, 18]

Once the activity of the hybrid catalysts towards benzene hydro-

genation is established, conditions would be modified for enhancing the ratio of cyclohexene to cyclohexane. Besides the factors which are typically varied in homogeneous reactions in order to determine the kinetics and mechanism of the active species (e.g., temperature, pressure of $H_2$, catalyst and reagent concentrations, addition of excess ligands, etc.) the heterogeneous nature of the catalysts allow a wider choice of solvents (or no solvent at all). Moreover, the contact time between the substrates and the catalysts can be varied over a wide range. Such experiments can provide mechanistic details concerning the intermediacy of cyclohexene and cyclohexadiene in the reaction as well as altering the product distribution from that determined by thermodynamics to one which also reflects the reaction kinetics. Hence, these studies would expand our understanding of the hydrogenation of aromatic compounds. Extensions to selective reductions of functionalized arene species could also be fruitful.

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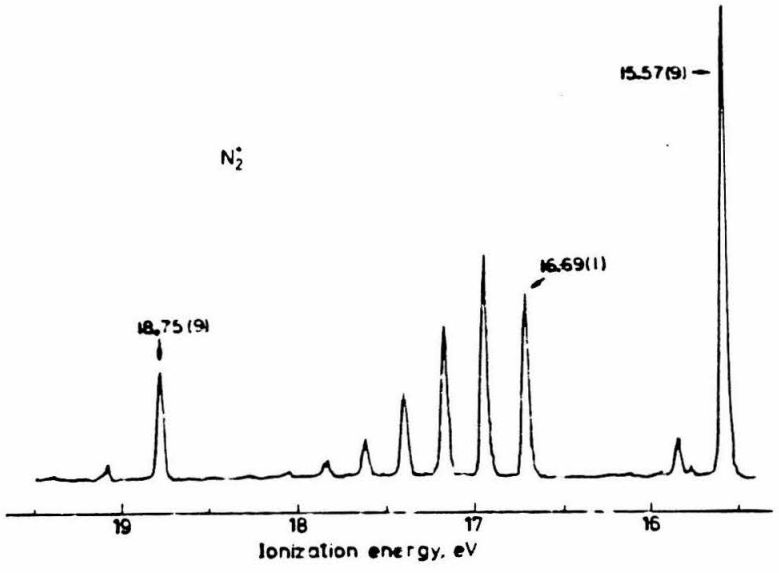
## PROPOSITION 3

A modest level of understanding has only recently been achieved in the field of metal surface chemistry.[1] Systematic study of the often unique reactions between adsorbed gases and metal surfaces has been closely coupled to major developments in instrumentation and experimental techniques as well as advances in theoretical chemistry. Presently the best characterized adsorbate-substrate systems involve the sorption of dioxygen, dinitrogen, dihydrogen, unsaturated hydrocarbons, or carbon monoxide on clean, well defined surfaces of platinum, nickel, tungsten, and iron. Surfaces of the other transition metals have been explored but their behavior with sorbed molecules remains poorly defined, as are the surface reactions of saturated hydrocarbons, oxides of nitrogen, and sulfur-containing compounds.[3] Utilizing the techniques of infrared and photoelectron spectroscopy, an investigation of the geometry and stability of sulfur dioxide adsorbed onto a vanadium surface is proposed.

A brief discussion of the characteristics of photoelectron spectroscopy (PES) may be helpful before dealing with the system of interest.[1b,4] Photoelectron spectroscopy involves the absorption of a photon of energy ($h\nu$) by a molecule and the measurement of the kinetic energy of the electron ($E_k$) which is subsequently ejected from an occupied orbital of that molecule. From this measurement and the use of a monochromatic photon source of known energy, the ionization energy of the electron, $I_i$, from a given orbital can be found from the relationship,

$$I_i = h\nu - E_k.$$

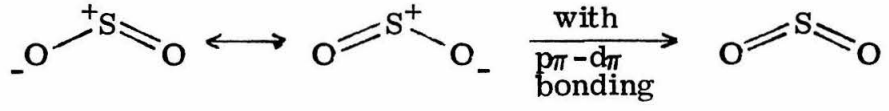
This conservation of energy equation may be modified to include ionization from molecular vibrational (and rotational) excited states which cause discrete shifts in $E_k$, yielding the equation $I_i = h\nu - E_k - \Delta E_v$. These shifts appear as fine structure in the bands and aid in the orbital assignments of the bands. For example, the PE spectrum of dinitrogen obtained by irradiation with the far ultraviolet light of the He I spectral line at 58.4 nm ($h\nu$ = 21.22 eV) displays changes in the vibrational spacings which reflect the removal of an electron from a slightly bonding orbital for the band at I = 15.6 eV, a strongly bonding orbital at 16.7 eV, and an antibonding orbital at 18.8 eV.




Photoelectron spectrum of nitrogen excited by He I radiation.

This interpretation is in accord with the qualitative molecular orbital (MO) scheme which may be drawn for $N_2$. (The PE spectrum reveals vibrational characteristics of the $N_2^+$ product rather than the initial $N_2$. Thus it is more reasonable to label PE spectra accordingly.[1b]) The proposed study will utilize ultraviolet photoelectron spectroscopy (UPS) to probe the outer shell or valence orbitals of the adsorbed species on vanadium. Electric and microwave discharge provide the most common sources of vacuum ultraviolet light, the He I and He II ($\lambda$ = 30.4 nm, $h\nu$ = 40.81 eV) lines being the most widely employed. X-rays (1-20 keV) may be used to ionize electrons from inner shell orbitals in an anlogous manner. This is the basis of the field of X-ray photoelectron spectroscopy (XPS).[5] XPS encompasses a number of techniques of major importance to the study of surfaces including ESCA and Auger spectroscopy. XPS will not be required for the proposed experiments, however. The experimental limitations of UPS in the study of gas phase and surface species, the most serious of which is the application of Koopmans' Theorem, will be discussed as they pertain to the specific $SO_2$-V system.

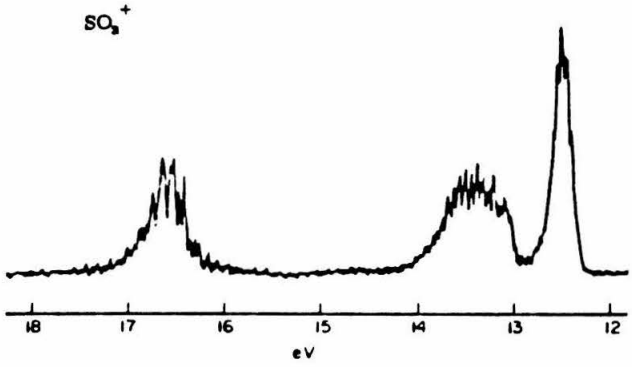
Sulfur dioxide is a nonlinear triatomic molecule with an OSO angle of 119.5°.[6] The valence bond representations involve $sp^2$ hybridization of the sulfur orbitals:




Back donation of electron density by the singly bonded oxygen into an empty 3d orbital of the sulfur is suggested[6b] for reducing the apparent

charge separation and accounting for the S–O bond energy (125 kcal/mol, comparable to 127 kcal/mol found for O=CO)[7] and bond length (1.432 Å, compared with the 1.45(2) Å S–O distance in $SOCl_2$).[8] The infrared spectrum[9] of $SO_2$ consists of a symmetric stretch ($\nu_1$) at 1151 $cm^{-1}$, a bending mode ($\nu_2$) at 518 $cm^{-1}$, and an antisymmetric stretch ($\nu_3$) at 1360 $cm^{-1}$.

The high resolution He I UP spectrum of $SO_2$ has been measured and assigned, based on the analysis of the vibrational fine structure.[10] Three strong bands are observed for $SO_2^+$ as shown below.

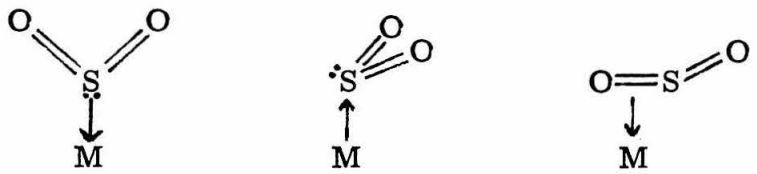



The lowest energy band at 12.30 eV is assigned to the sulfur lone pair orbital. Ionization of an electron from this orbital allows an increase in the OSO angle (as in $NO_2$) and results in a decrease of $\nu_2$ to 400 $cm^{-1}$. The second band between 13.0 and 13.8 eV is assigned to two ionization processes. With an origin at 13.01 eV, the oxygen $p_\pi$-sulfur $d_\pi$ bonding orbital exhibits the expected decrease in $\nu_3$ from 1360 to 1090 $cm^{-1}$. Overlapping with this is a nonbonding oxygen lone pair orbital which begins at 13.24 eV and possesses a vibrational splitting (500 $cm^{-1}$)

which is essentially the same as the infrared derived $\nu_2$ of $SO_2$. The third band between 16.0 and 17.2 eV is also attributed to ionization from two orbitals. In this instance both orbitals appear to be sulfur-oxygen bonding in character as evidence by decreases in the $\nu_1$ vibrational structuring from 1151 $cm^{-1}$ to 850 and 900 $cm^{-1}$ for the bands starting at 15.99 and 16.33 eV, respectively. Although there remains a question as to the relative ordering of the two bands, they have been assigned to the S–O $\pi$ and S–O $\sigma$ bonding orbitals.

Assignments based on theoretical calculations are similar to those derived from experiment.[11] The ordering of energetically similar orbitals (those within ca. 0.4 eV) is uncertain even in the best calculations, however. The approximations made in the theoretical calculations, that electronic and nuclear reorganizations do not take place while a molecule undergoes photoionization (Koopmans' Theorem) and that the energy and motion of each electron is independent (no electron correlation), introduce errors estimated to be about 1 eV in systems of this type.[1b] A loss in resolution also occurs in the UP spectra when the compounds are adsorbed onto surfaces, partly from losses in signal-to-noise. Surface infrared spectroscopy can furnish much of the lost vibrational information,[12] however, and relative errors between calculated orbital energies can be minimized from the additional information provided by comparisons between calculated and experimentally derived bond lengths and angles. Thus, the experimental UPS data on $SO_2$, aided by infrared and theoretical contributions, serve as the foundation for studying the reactivity of adsorbed sulfur dioxide.

The primary goal of the proposed research is the elucidation of the geometry of chemisorbed $SO_2$ on vanadium. While no $L_nV(SO_2)$ compounds ($L_n$ denotes other ligands) have been observed, three different geometries have been structurally characterized in other monomeric transition metal sulfur dioxide compounds;[13] sulfur bound and planar (I), sulfur bound and bent (II), and "edge-on" across one S–O double bond (III):




I II III

An oxygen bound geometry has also been observed for a sulfur dioxide complex of $SbF_5$.[14] Involvement of two or more metal sites add other possible geometries.[13,15] These structures can be distinguished by their differing effects on UPS band positions; for example, type I coordination would shift the sulfur lone pair orbital to higher energy in the UP spectrum relative to the other orbitals, whereas geometry III would shift the $p\pi$-$d\pi$ and S–O $\pi$ bands. Oxygen coordination could be clearly distinguished by a large shift in the oxygen lone pair band and smaller shifts for the S–O $\pi$ and $p\pi$-$d\pi$ bands. Corroborative information would be available from reflectance-absorbance infrared spectroscopy,[12] particularly for the bridging and chelating structures. This approach has been successfully used in studies on the adsorption of CO on W,[16] among others. The very basic question of how sulfur dioxide

is adsorbed on a vanadium surface can therefore be answered.

Complications due to vanadium's affinity for oxygen and to a lesser extent sulfur must be recognized. These problems may be overcome by working at low temperatures and high adsorbate coverages since a considerable activation energy is expected for the breaking of the S–O double bonds, particularly if few vacant sites are available. Determination of the temperature dependent stability of $SO_2$ on V comprises the remaining portion of this proposal. The formation of metal sulfate species has been observed for $SO_2$ on Fe and Ni,[3] and would be expected as the vanadium-sulfur dioxide system is warmed. At still higher temperatures, V–O and V–S species resulting from the dissociation of the $SO_2$ and $SO_4^{2-}$ may be observed. Again UPS and infrared techniques can be used to characterize these processes.

A fundamental understanding of the interaction of sulfur dioxide on a vanadium surface would be gained from this study. This information is necessary for studying the oxidation reaction of $SO_2$ by $O_2$ on vanadium or vanadium oxide surfaces, a problem of considerable complexity but one which is of great environmental and industrial importance.

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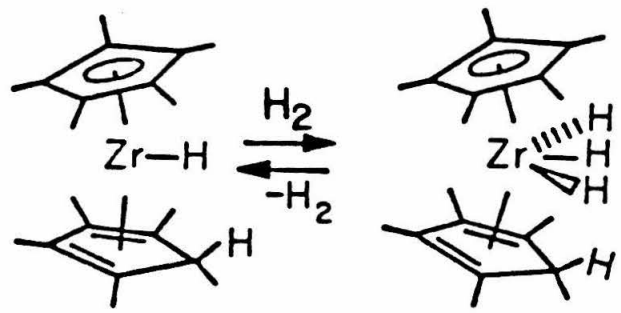
## PROPOSITION 4

Studying the reaction of $H_2/D_2$ with $Cp^*_2ZrH_2$ and $Cp^*_2Zr(H)R$, where $Cp^* = C_5(CH_3)_5$ and $R = CH_2CH(CH_3)_2$, Bercaw and coworkers[1] have proposed a mechanism involving the transfer of hydrogen from the metal to the $Cp^*$ ring to form a key $\eta^4$-cyclopentadiene zirconium(II) intermediate which can oxidatively add dihydrogen:




(1)

While the validity of this mechanism remains the subject of some controversy,[2] the mechanism does underscore the fact that little is known of the behavior of early transition metal $\eta^4$-cyclopentadiene complexes. An investigation of the reactivity of a niobium $\eta^4$-cyclopentadiene complex is proposed.

The rearrangement of $\eta^4$-cyclopentadiene metal complexes to the corresponding $(\eta\text{-}C_5H_5)MH$ species has been postulated or established for M = Fe,[3] Ru,[4] Os,[4] Re,[5] Cr,[6] Mo,[6] and W.[6] A related process, reversible hydrogen shifts, has been directly observed on the NMR timescale for $IrH(1,3\text{-}C_6H_8)_2$,[7] $IrH(1,3\text{-}C_6H_8)(1,5\text{-}C_8H_{12})$,[7] and ($\eta^4$-2,3-dimethyl-1,3-butadiene)$CoH(PPh_3)_2$.[8] It is interesting that the fluxional process for these cobalt and iridium complexes which moves

a hydrogen from the metal to the diene ligand, does not involve any changes in the formal oxidation state of the metal centers. This is in contrast to the proposal set forth for $Cp^*_2ZrH_2$.

Photochemical substitution of $CpNb(CO)_4$ in cyclopentadiene/pentane affords $CpNb(\eta^4\text{-}C_5H_2)(CO)_2$ in good yield (eq. 2)[9] which apparently[10] undergoes thermal loss of one carbon monoxide ligand and hydrogen migration from the $C_5H_6$ ring to the niobium to form $Cp_2NbH(CO)$ (eq. 3).

$$CpNb(CO)_4 + C_5H_6 \xrightarrow{h\nu} Cp(C_5H_6)Nb(CO)_2 + 2CO \qquad (2)$$

$$Cp(C_5H_6)Nb(CO)_2 \xrightarrow{\Delta} Cp_2NbH(CO) + CO \qquad (3)$$

The stability of the dicarbonyl diene complex suggests that carbonylation of $Cp_2NbH(CO)$ or the corresponding trialkylphosphine hydride, $Cp_2NbH(PR_3)$,[11] would bring about metal to ring hydrogen migration, establishing the reaction in equation as reversible (eq. 4).

$$CpNb(C_5H_6)(CO)(L) \rightleftharpoons Cp_2NbH(CO) + L \qquad (4)$$

where $L = CO, PR_3$

Entry into this class of complexes can be made via the chlorocarbonyl, $Cp_2NbCl(CO)$,[12] thus allowing the synthesis of the specifically labelled compound $Cp_2NbD(CO)$. The thermolysis of the deutero carbonyl with and without added ligand L, could establish a lower limit for the rate of hydrogen (deuterium) migration to the ring, provided a crossover experiment demonstrates that any H-D exchange is due to intramolecular processes.

Photolysis of $CpNb(CO)_4$ in the presence of $C_5Me_5H$ should initially give $CpNb(C_5Me_5H)(CO)_2$ which may exist as a pair of isomers, one with an endo methyl group, the other exo. If no other isomerizations occur, the exo methyl isomer would be expected to undergo ring to metal hydrogen migration faster than would the endo isomer. Again deuterium labelling, in this case on the $C_5H_5$ ring, may provide evidence of subsequent hydrogen migration from the product $(C_5D_5)(C_5Me_5)NbH(CO)$. More detailed information could be obtained by measuring the kinetics of these reactions, provided the reactions proceed cleanly.

The study of niobium $\eta^4$-cyclopentadiene complexes will probably contribute little to the resolution of the question of how dihydrogen interact with $(C_5Me_5)_2ZrH_2$. However, it should prove valuable for exploring the stability and reactivity of a poorly explored class of early transition metal compounds.

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## PROPOSITION 5

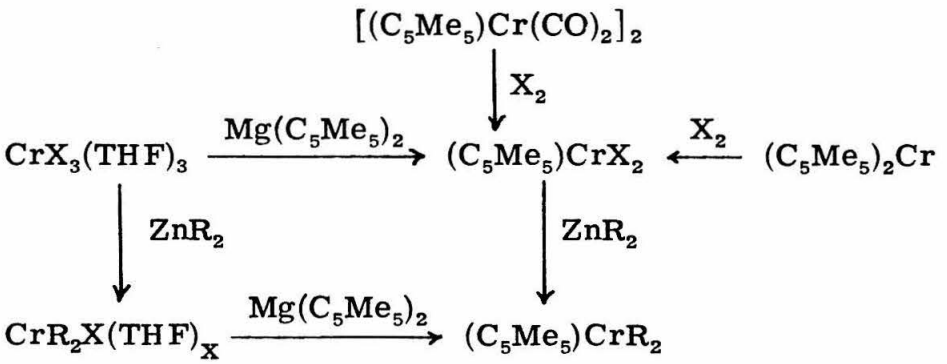
Little is known about the organometallic chemistry of chromium in its high formal oxidation states. Only a single class of Cr(IV) compounds, tetra(alkyl)Cr(IV), has been investigated[1] and there are no reports of organochromium(V) or (VI) species in the literature. Even Cr(III) systems remain poorly explored when compared with the organic derivatives of chromium (0), (I), and (II) which have been extensively studied and have been found to exhibit a wealth of interesting chemistry.[2] The limited data which are available, however, do suggest that highly oxidized organochromium compounds would be interesting systems for investigating a number of fundamentally important problems. Utilizing ligands such as the pentamethylcyclopentadienyl anion to provide sufficient steric bulk and electron donation to stabilize these unusual oxidation state species, experiments involving the synthesis and mechanistic study of organochromium(III) and (IV) complexes are proposed.

Plausible routes for the preparation of a basic class of dialkyl derivatives of Cr(III), $(\eta\text{-}C_5Me_5)CrR_2$, are shown in the Figure. The known pentamethylcyclopentadienyl chromium dicarbonyl dimer[3] and decamethylchromocene[4] would serve as convenient sources of the $(C_5Me_5)Cr$ moiety. The oxidation and alkylation reactions shown have been observed for the parent $C_5H_5$ or trialkyl complexes.[5] Studies with compounds such as $(C_5Me_5)Cr(CH_2CMe_3)_2$ would seek to establish mechanism(s) of metal-carbon bond cleavage. Hydrogen abstraction,[5c] homolytic bond scission,[6] and dinuclear processes[6] have all been

observed with Cr(III) alkyls.

Oxidation reactions of the $(C_5Me_5)CrR_2$ and the corresponding trialkyl anions to the Cr(IV) species, $(C_5Me_5)CrR_3$,[1] and perhaps to Cr(V) complexes will be explored. The latter would be expected to be quite reactive and the mechanism of decomposition would likely involve reductive elimination of R-R. By analogy to the tetraalkylchromium(IV) compounds, the $(C_5Me_5)CrR_3$ species are expected to exhibit moderate stability for R = $CH_2CMe_3$ and $CH_2CMe_2Ph$.[1] Treatment of these complexes with unsaturated substrates such as carbon monoxide, dihydrogen, olefins, and oxygen could uncover some unusual reactivity, since the complexes are formally sixteen electron, $d^2$ species, yet are not expected to react via oxidative addition pathways. Preparation of the organochromium(IV) complexes may also use the Cr(IV) tetraalkoxide and tetramide complexes.[7] This route offers the potential of forming mixed Cr(IV) alkylamide and alkylalkoxide complexes.

It is hoped that these experiments will serve as a basis for uncovering and developing new patterns of early transition metal reactivity.



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